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Copper-Induced Corrosion of  
Galvanized Steel Pipe

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COPPER-INDUCED CORROSION OF GALVANIZED STEEL PIPE

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| 16. ABSTRACT<br>An investigation was conducted to determine the cause(s) of rapid pitting failure of galvanized steel pipe used in consumer plumbing systems. The presence of copper in water and the character of the galvanized steel pipe were factors examined in detail. Pipe manufactured in Korea, Australia, and in the U.S. were compared for pipe structure and zinc coating. The pipe manufactured in Korea by electrical resistance welding had a pronounced weld seam, whereas U.S. and Australian pipes manufactured with butt welding had only small or nonexistent seams. Furthermore, the zinc coating on the Korean pipe failed to meet the weight-of-coating standard (1.8 oz/ft <sup>2</sup> ) in 11 of 14 samples. Examination of the iron/zinc interface on the Korean pipe revealed possible sites of poor adhesion of the coating to the base metal.<br>In pilot testing, increasing copper concentrations (from 0.0 to 5.0 mg/L) produced increased corrosion activity on the pipe surface as measured by greater deposition of scale, calcium, iron, zinc, and copper. Also, the ratio of iron surface area to zinc surface area increased. Other factors, such as the mode of exposure and the addition of citrate, had no measurable impact. The corrosion activity, as measured by scale formation, was greatest on the Korean pipe, followed by the U.S. and Australian. Rapid pitting of the sort observed in several southern California homes did not occur under any of the conditions tested. |                                                  |                              |
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## FOREWORD

The U. S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

The present study addresses the problem of pitting corrosion in galvanized steel pipe used in consumer plumbing systems. The presence of copper in water and the character of galvanized steel pipe were factors examined in detail. The information presented in this report provides a more scientific basis for dealing with problems of corrosion in water distribution systems.

Francis T. Mayo, Director  
Water Engineering Research Laboratory

## ABSTRACT

An investigation was conducted to determine the cause(s) of rapid pitting failure of galvanized steel pipe used in consumer plumbing systems. The presence of copper in water and the character of the galvanized steel pipe were factors examined in detail.

Pipe manufactured in Korea, Australia, and in the U.S. were compared for pipe structure and zinc coating. The pipe manufactured in Korea by electrical resistance welding had a pronounced weld seam, whereas U.S. and Australian pipes manufactured with butt welding had only small or nonexistent seams. Furthermore, the zinc coating on the Korean pipe failed to meet the weight-of-coating standard (1.8 oz/ft<sup>2</sup>) in 11 of 14 samples. Examination of the iron/zinc interface on the Korean pipe revealed possible sites of poor adhesion of the coating to the base metal.

In pilot testing, increasing copper concentrations (from 0.0 to 5.0 mg/l) produced increased corrosion activity on the pipe surface as measured by greater deposition of scale, calcium, iron, zinc, and copper. Also, the ratio of iron surface area to zinc surface area increased. Other factors, such as the mode of exposure and the addition of citrate, had no measurable impact. The corrosion activity, as measured by scale formation, was greatest on the Korean pipe, followed by the U.S. and Australian. Rapid pitting of the sort observed in several southern California homes did not occur under any of the conditions tested.

The work described in this project report was performed by James M. Montgomery, Consulting Engineers, Inc. as subcontractor to the Metropolitan Water District of Southern California. This report was submitted in fulfillment of Contract No. CR 807446-02 by the Metropolitan Water District of Southern California under the partial sponsorship of the U.S. Environmental Protection Agency and covers a period from December 1980 through February 1984.

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## LIST OF ABBREVIATIONS

### Abbreviations

|      |                                                    |
|------|----------------------------------------------------|
| ASTM | American Society of Testing Materials              |
| CPVC | chlorinated polyvinyl chloride                     |
| CRW  | Colorado River water                               |
| EDX  | energy dispersive X-ray                            |
| JMM  | James M. Montgomery, Consulting Engineers, Inc.    |
| L    | liter                                              |
| mg   | milligram                                          |
| ml   | milliliters                                        |
| mv   | millivolts                                         |
| MWD  | Metropolitan Water District of Southern California |
| PVC  | polyvinyl chloride                                 |
| SEM  | scanning electron microscopy                       |
| SWP  | State water project                                |
| TDS  | total dissolved solids                             |

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In addition, valuable input to the project was received from Dr. James Morgan of the California Institute of Technology, Dr. Francis Donahue of the University of Michigan, Dr. Jerome Thomas of the University of California at Berkeley and Mr. Robert Lewis Ray of Berkeley, California.

## SECTION 1

### INTRODUCTION, CONCLUSIONS AND RECOMMENDATIONS

#### INTRODUCTION

Over the past two decades, several occurrences of accelerated pitting corrosion of small-diameter, galvanized steel pipe have been investigated by Cruse<sup>(1)</sup>, Trussell<sup>(2)</sup>, and Treweek<sup>(3)</sup>. Pitting is a term used to describe a form of corrosion wherein a concentrated attack occurs at small sites, often perforating the pipe (Figure 1). Pitting typically causes leaks and destroys a pipe's usefulness long before the end of its rated economic life. Recent episodes of this type of corrosion have taken place in large housing tracts where widespread pitting failure of household plumbing occurred within five years of construction.

Several factors have been alleged to cause or enhance the corrosion problem, including the presence of copper in the water, the surface character of the pipe, base metal and/or zinc coating composition and integrity, and water temperature and quality. Cruse<sup>(1)</sup> was the first to collect and correlate data on various instances of this type of corrosion in the southern California area. He concluded that the common factor in failures which occurred in a variety of water sources, building types, and in both hot and cold waters, was the presence of copper in the water. Subsequent investigations into housing tract failures by Trussell<sup>(2)</sup> and Treweek<sup>(3)</sup> seemed to bear out this hypothesis. Table 1 summarizes the conditions observed and failures investigated by each of these three workers. As shown in Table 1, the latter four cases involved housing tracts with up to 500+ units affected. Copper in the water was associated with each case, either via its use as an algicide or through dissolution of copper piping. The variety of water sources included local well water, low TDS Owens River water, and high TDS Colorado River water (CRW).

To further investigate the factors which are important in this type of corrosion, a cooperative research agreement was established between the U.S. Environmental Protection Agency (EPA) and the Metropolitan Water District of Southern California (MWD) with James M. Montgomery, Consulting Engineers, Inc. (JMM) subcontracted to assist MWD. Under the agreement, a pilot-scale facility was designed, constructed, and operated in which the effects of copper dose, pipe type, mode of exposure of the pipe to test solutions, and water quality could be tested over a period of three years. During that period, ancillary bench and laboratory studies were also carried out on the effects of pipe structure, iron-zinc polarity reversal, and pipe surface anomalies was also carried out. This report contains findings made in each of these areas.

#### CONCLUSIONS

The first phase of this investigation concentrated on determining the characteristics of the galvanized steel pipe structure and the zinc coating. The results

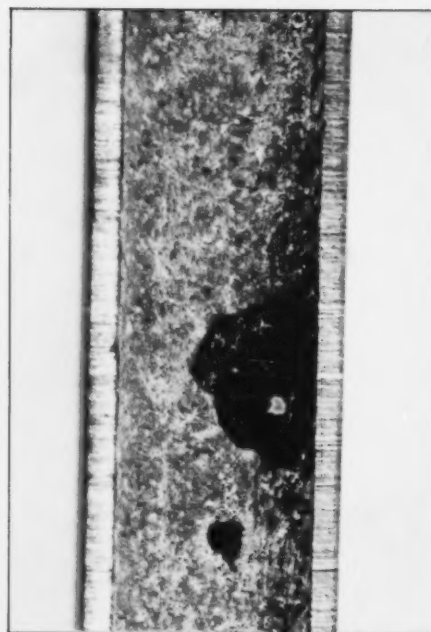


Figure 1a. New sections of 3/4" ASTM A A-120 galvanized steel pipe.

Figure 1b. Pitted pipe removed from housing tract where numerous early failure of piping occurred.



TABLE I  
SUMMARY OF COPPER-RELATED CORROSION OF GALVANIZED STEEL WATER PIPES

| Affected Units             | Year | Source of Water Supply           | Source of Copper                | Copper Concentration in Water (mg/l) | Surface Copper Concentration on Pipe (mg/dm <sup>2</sup> ) | Corrective Action Recommended                                                                                                                        | Comment                                                                                                                  |
|----------------------------|------|----------------------------------|---------------------------------|--------------------------------------|------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------|
| Apartment Houses (94)      | 1961 | Local wells and Colorado River   | Reservoir algicide              | N/A                                  | 12-25                                                      | Install new copper pipes. Discontinue the use of CuSO <sub>4</sub> algicide. Reduce dissolved O <sub>2</sub> by blending                             | Pipe failure via pitting corrosion in 18-36 months                                                                       |
| Lodge (75 units)           | 1962 | Local wells                      | Reservoir algicide              | N/A                                  | 11-26                                                      | Reduce reservoir aeration, reduce intake of highly mineralized water, reduce hot water temperature,                                                  | Hot (140-160°F) water system<br>Pipe failure via pitting corrosion in 18 months                                          |
| Motel (21 units)           | 1965 | Local wells                      | Dissolution of copper pipe      | 0.01-0.08                            | 0.84                                                       | Reduce velocity of circulation, avoid mixing of copper and iron piping systems, continue polyphosphate treatment                                     | Circulating hot (150°C) water system. Red water and iron particles from pitting corrosion in 18 months                   |
| Apartment Hotel (44 units) | 1968 | Owens Valley                     | Copper tubes in heat exchangers | 0.05                                 | 9.6                                                        | Replace corroded galvanized steel hot water piping with copper system                                                                                | Circulating hot (130°F) water system. Pipe failure via pitting corrosion in 108 months                                   |
| Tract Homes (39 units)     | 1973 | Local wells                      | Reservoir algicide              | 0.029-0.063                          | Not analyzed                                               | Adjust pH to positive Langelier Index, aerate supply to remove hydrogen sulfide, cease use of polyphosphate inhibitor, discontinue CuSO <sub>4</sub> | Pipe failure via pitting corrosion in 24-36 months                                                                       |
| Tract Homes (100+ units)   | 1973 | Colorado River                   | Reservoir algicide              | 0.1-0.5                              | Not analyzed                                               | Replace galvanized pipe with copper pipe. Use greater care in application of copper sulfate-citric acid complex as algicide                          | Pipe failure via pitting corrosion in 12-24 months                                                                       |
| Tract Homes (500+ units)   | 1977 | Colorado River                   | Reservoir algicide              | 0.01-0.4                             | 15-34                                                      | Replace galvanized pipe with copper pipe. Use greater care in application of copper sulfate-citric acid complex as algicide                          | Pipe failure via pitting corrosion in 12-24 months                                                                       |
| Tract Homes (340 units)    | 1978 | Colorado River & Northern Calif. | Reservoir algicide              | 0.3-4.3                              | 2.5-12.3                                                   | Replace galvanized pipe with copper pipe                                                                                                             | Pipe failure via pitting corrosion within 24-60 months. 90% of leaks in horizontal pipes, 72% of leaks in hot water pipe |

of this first phase of investigation are summarized in Table 2. With respect to the elemental composition of the base metal, emission spectroscopy determined that the base steel utilized by each of the three manufacturers (Australian, Korean, and U.S.), were satisfactory for trace elements in the steel. The Korean pipe had a lower carbon content than either the Australian or the U.S. pipe, but this should not affect its corrosion potential. Microscopic examination of a cross-section of Korean pipe revealed a pronounced weld seam, probably produced during electrical resistance welding, whereas the U.S. and Australian pipes had only a small or non-existent seam, respectively. The weld seam on the Korean pipe produced a discontinuity in the otherwise smooth interior surface.

The zinc coating on pipe samples from each of the three manufacturers was examined by energy dispersive X-ray (EDX) to determine the elemental composition of the zinc/iron layers at the interface. No abnormal components were found in any of the three layers which consisted primarily of zinc and iron, with trace amounts of lead. The thickness of the zinc coating was determined by three tests: weight of coating test (ASTM A90-81), Preece test (ASTM A239-73), and microscopic examination. The Korean pipe failed to meet the weight of coating standard (1.8 oz/ft<sup>2</sup>) in 11 of 14 samples. The Australian and U.S. pipes met this standard in all instances. In the Preece test, 12 of the 14 Korean pipe samples required only one dip in copper sulfate solution to reveal the base metal. Ten of the 14 Australian pipe samples required two to three dips to reveal the base metal and 12 of the 14 U.S. pipe samples required more than two dips to reveal the base metal. As would be expected from the weight of coating test and the Preece test, the microscopic examination of three samples revealed that the total zinc coating on the Korean pipe was the thinnest. Furthermore, each of the three layers which make up the zinc/iron innerface (the delta, zeta, and eta layers) were thinner for the Korean pipe than for the Australian or U.S. pipe. From these three tests, a picture emerged of the Australian pipe having a uniform, smooth coating having the proper thickness, the Korean pipe having a uniform thin coating with occasional blemishes, and the U.S. pipe having a more variable but thick coating with occasional blemishes and irregularities.

Subsequent etching and microscopic examination of the iron/zinc innerface on all three pipes revealed sites of poor adhesion of the zinc coating to the base metal on the Korean pipe. In some instances, a thin gap appears to exist between the zinc coating and the underlying base metal.

Because premature pitting failure of galvanized pipe has been demonstrated to occur due to potential reversal between the iron and zinc, bench-scale testing was conducted to determine if such potential reversal was occurring at the elevated temperatures of hot water systems. Additional tests were run to determine if unusual corrosion would occur at specially created pipe surface anomalies. The results of the bench-scale testing are summarized in Table 3. As shown, potential reversal occurred in the water solution matched to that which had been used by earlier investigators. For water supplies currently available in southern California, however, (the two surface water sources, State Water Project and Colorado River water, and one groundwater source, Pasadena tap water) no potential reversal occurred over the temperature range and time interval tested.

Pipe surface anomalies were created on Korean galvanized steel pipe by acid etching and/or by drilling a small hole into the zinc layer. While localized corrosion was enhanced in the drilled areas, the acid etching of the zinc surface had no

TABLE 2  
SUMMARIZED CHARACTERISTICS OF GALVANIZED STEEL PIPE  
STRUCTURE AND COATING

| Characteristic                  | Pipe Manufacturer                                           |                                                                           |  | U.S.                                                         |
|---------------------------------|-------------------------------------------------------------|---------------------------------------------------------------------------|--|--------------------------------------------------------------|
|                                 | Australian                                                  | Korean                                                                    |  |                                                              |
| Pipe Structure                  |                                                             |                                                                           |  |                                                              |
| Base Metal Chemical Composition |                                                             |                                                                           |  |                                                              |
| Fabrication Anomalies           | Satisfactory<br>None                                        | Satisfactory<br>Pronounced weld seam                                      |  | Satisfactory<br>Slight weld seam                             |
| Pipe Coating                    |                                                             |                                                                           |  |                                                              |
| Thickness                       | Uniform coating<br>All samples > 1.8 oz/ft <sup>2</sup>     | Uniform coating<br>11 of 14 samples < 1.8 oz/ft <sup>2</sup><br>Blemishes |  | Variable coating<br>All samples > 1.8 oz/ft <sup>2</sup>     |
| Weight of Coating Test          | Uniform, smooth coating<br>2 to 3 dips for 10 of 14 samples | 1 dip for 12 of 14 samples                                                |  | Variable coating<br>More than 2 dips for<br>12 of 14 samples |
| Preece test                     | Average coating                                             | Thin coating                                                              |  | Thick coating                                                |
| Microscopic test                | Satisfactory                                                | Satisfactory                                                              |  | Satisfactory                                                 |
| Chemical Composition            |                                                             |                                                                           |  |                                                              |
| Adhesion                        | Satisfactory                                                | Separation zone between base<br>metal and coating                         |  | Satisfactory                                                 |

TABLE 3  
RESULTS FOR BENCH-SCALE TESTING FOR POTENTIAL REVERSAL  
AND UNUSUAL CORROSION AT PIPE SURFACE ANOMALIES<sup>1</sup>

| Characteristic                                | Water Source               |                   |                            |                           |                                |                                         |
|-----------------------------------------------|----------------------------|-------------------|----------------------------|---------------------------|--------------------------------|-----------------------------------------|
|                                               | Control Water <sup>2</sup> | SWP <sup>3</sup>  | CRW <sup>4</sup>           | Pasadena Tap <sup>5</sup> |                                |                                         |
| 1. Potential Reversal                         | Reversal occurred          | No reversal       | No reversal                | No reversal               |                                |                                         |
| Distilled Water Plus Constituent <sup>6</sup> |                            |                   |                            |                           |                                |                                         |
|                                               | Control                    | CuSO <sub>4</sub> | Citrated CuSO <sub>4</sub> | Cu Plated                 |                                |                                         |
| 2. Water Quality Impact                       |                            |                   |                            |                           |                                |                                         |
| Pipe Surface Anomalies                        |                            |                   |                            |                           |                                |                                         |
| Control                                       | None                       | None              | None                       | None                      |                                |                                         |
| Acid etched                                   | None                       | None              | None                       | None                      |                                |                                         |
| Acid etched and drilled                       | Localized                  | Localized         | Localized                  | Localized                 |                                |                                         |
| Drilled                                       | Localized                  | Localized         | Localized                  | Localized                 |                                |                                         |
| Pasadena Tap Plus Constituent <sup>5</sup>    |                            |                   |                            |                           |                                |                                         |
|                                               | Control                    | CuSO <sub>4</sub> | Citrated CuSO <sub>4</sub> | Azurite                   | CuSO <sub>4</sub> with Azurite | Citrated CuSO <sub>4</sub> with Azurite |
| 3. Pipe Surface Anomalies                     |                            |                   |                            |                           |                                |                                         |
| Control                                       | None                       | None              | None                       | Zinc loss                 | Zinc loss                      | Zinc loss                               |
| Acid etched                                   | None                       | None              | None                       | Zinc loss                 | Zinc loss                      | Zinc loss                               |
| Drilled                                       | None                       | None              | None                       | Zinc loss                 | Zinc loss                      | Zinc loss                               |
| Black iron                                    | Generalized                | Generalized       | Generalized                | Generalized               | Generalized                    | Generalized                             |

<sup>1</sup> All tests utilized Korean galvanized pipe samples except as noted.

<sup>2</sup> Distilled water plus 110 mg/l HCO<sub>3</sub>, 10 mg/l SO<sub>4</sub>, 10 mg/l NO<sub>3</sub>

<sup>3</sup> State Water Project

<sup>4</sup> Colordao River Water

<sup>5</sup> Local groundwater source

<sup>6</sup> The same tests but with salts added to create high TDS (2000 mg/l) water showed no localized corrosion.

measurable impact. Similarly, the addition of copper sulfate or citrated copper sulfate to the solution did not noticeably increase the localized corrosion over that recorded for the control, which consisted of distilled water. Copper plating portions of the sample, both clean and clean with acid etching had little effect. Similar results were recorded when Pasadena tap water was substituted for distilled water. Azurite crystals placed on the bottom of the interior pipe surface did accelerate the loss of zinc from the surface. In general, the addition of copper sulfate or citrated copper sulfate did not have an obvious corrosion impact different than that from the control solution without these chemicals.

Pilot plant testing was undertaken to determine the impact of five major variables: copper dose (0.0 to 5.0 mg/L), pipe manufacturer (Australian, Korean, U.S.), initial mode of exposure (static, flowing), water quality (CRW, SWP), and complexing agent (citrated, uncitrated) on the corrosion rate of galvanized steel pipe. Table 4 is a summary of the results of this pilot plant testing.

Pipes from all three countries were exposed to CRW water for up to 20 months and increasing copper doses from 0.0 to 5.0 mg/L. The effect on the galvanized steel pipe was determined by measuring the extent of scale, calcium, iron, zinc, and copper deposition on the interior pipe surface. In addition, the iron to zinc ratio was determined for the interior surface area after the scale had been removed. Irrespective of the pipe manufacturer, increased copper doses invariably led to increased scale as well as increased iron to zinc ratios. Increasing the exposure time from eight to 20 months generally resulted in overall increased scale deposition, although the amount of calcium in the scale showed no difference. The iron to zinc ratios also showed no consistent increase with increased exposure time. Finally, the mode of exposure, (static vs. flowing test solution) made no apparent difference on the extent of corrosion.

As with the CRW experiment, pipes from all the manufacturers exposed to SWP water with increasing doses of copper produced increasing deposition on the interior pipe surface. As the copper dose increased from 0.0 to 5.0 mg/L the scale, calcium, iron, zinc, and copper deposition on the interior pipe surface similarly increased. The iron to zinc ratio of the surface exposed also increased. The addition of 2.5 mg/L of citrate to the solution containing 5.0 mg/L of copper produced no apparent difference compared to the solution containing just 5.0 mg/L of copper. Finally, the mode of exposure (static vs. flowing test solution) showed no difference in terms of the extent of corrosion.

The results from eight months exposure to CRW were compared with those from seven months exposure to SWP for all the pipe manufacturers. At each copper dose, the scale formed in the CRW supply was greater than the scale formed in the SWP supply, a result expected from the more positive Langelier Index of the CRW supply. The extent of zinc removal and deposition varied among the different pipe manufacturers with no consistent pattern, while the extent of copper deposition was always less from the CRW supply than from the SWP supply. The iron to zinc ratios for the exposed surface area indicated that the CRW supply was at least as aggressive in removing the zinc layer as the SWP and in some instances, more aggressive.

With respect to the different pipe manufacturers, the Korean pipe generally produced the greatest scale, calcium, zinc, and copper deposition while the U.S. pipe deposition was between that of the Korean and Australian samples. The U.S. pipe



TABLE 4  
RESULTS OF PILOT PLANT TESTING OF CORROSION OF  
GALVANIZED STEEL PIPE<sup>1</sup>

1. Colorado River Water Exposure

| Test Conditions                         | Effect on Pipe      |                       |                        |                        |                      |                             |
|-----------------------------------------|---------------------|-----------------------|------------------------|------------------------|----------------------|-----------------------------|
|                                         | Scale<br>Deposition | Calcium<br>Deposition | Iron<br>Deposition     | Zinc<br>Deposition     | Copper<br>Deposition | Surface<br>Exposed<br>Fe/Zn |
| Increase Cu dose (0.0 to 5.0 mg/l)      | Increase            | Increase              | Increase               | Increase               | Increase             | Increase                    |
| Increase exposure time (8 to 20 months) | Increase            | Unchanged             | Increase               | Increase               | Increase             | Variable                    |
| Mode of exposure (static vs flowing)    |                     |                       | No apparent difference | No apparent difference |                      |                             |
| Section of pipe (top or bottom)         |                     |                       | No apparent difference | No apparent difference |                      |                             |

2. State Water Project Exposure

| Test Conditions                               | Effect on Pipe      |                       |                        |                        |                      |                             |
|-----------------------------------------------|---------------------|-----------------------|------------------------|------------------------|----------------------|-----------------------------|
|                                               | Scale<br>Deposition | Calcium<br>Deposition | Iron<br>Deposition     | Zinc<br>Deposition     | Copper<br>Deposition | Surface<br>Exposed<br>Fe/Zn |
| Increase Cu dose (0.0 to 5.0 mg/l)            | Increase            | Increase              | Increase               | Increase               | Increase             | Increase                    |
| Addition of citrate (2.5 mg/l to 5.0 mg/l Cu) |                     |                       | No apparent difference | No apparent difference |                      |                             |
| Mode of exposure (static vs flowing)          |                     |                       | No apparent difference | No apparent difference |                      |                             |

3. Comparison of CRW (8 months exposure) with SWP (7 months exposure)

| Test Conditions                    | Effect on Pipe      |                       |                    |                    |                      |                             |
|------------------------------------|---------------------|-----------------------|--------------------|--------------------|----------------------|-----------------------------|
|                                    | Scale<br>Deposition | Calcium<br>Deposition | Iron<br>Deposition | Zinc<br>Deposition | Copper<br>Deposition | Surface<br>Exposed<br>Fe/Zn |
| Increase Cu dose (0.0 to 5.0 mg/l) | CRW > SWP           | CRW > SWP             | CRW > SWP          | Variable           | CRW < SWP            | CRW $\geq$ SWP              |

4. Comparison of Pipe Manufacturers

| Test Conditions                    | Effect on Pipe      |                       |                    |                    |                      |                             |
|------------------------------------|---------------------|-----------------------|--------------------|--------------------|----------------------|-----------------------------|
|                                    | Scale<br>Deposition | Calcium<br>Deposition | Iron<br>Deposition | Zinc<br>Deposition | Copper<br>Deposition | Surface<br>Exposed<br>Fe/Zn |
| Increase Cu dose (0.5 to 5.0 mg/l) | K > US > A          | K > US > A            | US > K > A         | K > US > A         | K > US > A           | Variable                    |

<sup>1</sup> All tests were carried out using the pipe from Korea, Australia and the U.S.



appeared to produce the greatest iron deposition, with the Korean pipe between the U.S. and Australian samples. The iron to zinc ratio of exposed surface area was variable between the different pipe manufacturers, with no consistent pattern.

The pilot plant testing demonstrated increased corrosion activity associated with two variables, increasing copper dose (0-5 mg/L) and pipe manufacturer (Korean pipe showed the most corrosion and Australian the least). This corrosion activity was evidenced by the removal of zinc and iron from the pipe surfaces and the formation of deposits containing calcium, iron, zinc and copper. Pits which did occur on the pipe surfaces were scattered over the entire surface of the pipe and were generally superficial, never becoming deep enough to warrant depth measurement. During the two years of pilot testing, no deep isolated pits of the type which originally motivated the study were observed. It is not clear if a longer test period or more severe test conditions, such as longer exposure time in hot water would have resulted in eventual pitting failure.

#### RECOMMENDATIONS

Given past observations of the influence of copper on galvanized steel pipe and our findings regarding the differences in pipe quality among Korean, U.S., and Australian pipe, these results are unexpected. Based on the galvanic series, copper is known to be aggressive to less noble metals such as zinc and iron, and pitting failure of galvanized recirculating hot water systems due to copper contamination is quite common. The large scale pitting failures found in houses during field studies and which precipitated this study appeared to match the failures of the recirculating hot water systems. However, our testing of copper in both pilot and bench-scale facilities, and coupled with a host of other variables did not demonstrate this phenomenon. Use of Korean pipe with its substandard zinc coating did not produce this result either. Thus the recommendations below are directed towards re-evaluating field occurrences of this type of corrosion and attempting to determine if flaws in the experimental designs of the pilot plant and bench tests precluded expected results.

1. Retain samples from bench and pilot testing for further analyses. Of specific concern is whether the rapid scale build-up on the pipe during the pilot testing interfered with the action of copper on the pipe surfaces.
2. In this same context, a comparison of the form of copper which was precipitated on the pilot plant pipes to copper found on pipes which have failed in the field in housing tracts and in recirculating hot water systems seems warranted. It is possible that the pilot plant conditions resulted in a precipitate which is less intensively corrosive than that observed under these other conditions.
3. Provide more thorough scrutiny of the conditions under which failures in housing tracts occurred and may occur in the future. It would be useful to have a group of experts from several fields such as chemistry, metallurgy, and corrosion, and who are familiar with the problem, examine any future occurrences and concur as to the significant variables.

## SECTION 2

### TECHNICAL APPROACH

The technical approach taken in carrying out this research was on three levels: (1) laboratory evaluation of pipe structure and manufacture, (2) bench studies to evaluate the effect of pipe surface anomalies and the possibility of potential reversal between the iron and zinc layers of the pipe, and (3) pilot plant studies to evaluate the relative effects of copper dose, pipe type, mode of exposure, and water quality in instigating pitting type corrosion. All work was carried out utilizing ASTM A-120 galvanized steel pipe. This terminology refers to the American Society of Testing and Materials' specifications which outline characteristics that pipe used for household water transport should meet. This chapter presents a brief overview of the methods utilized for each segment of work; further details are contained within subsequent chapters.

#### PIPE STRUCTURE AND MANUFACTURE

The pipe structure and manufacture was evaluated for any inherent potential to make the pipe more or less susceptible to corrosion. Within this context, three types of pipe were considered: U.S., Korean, and Australian. The samples from each country were from single manufacturers; thus results obtained should not be construed as applying to all manufacturers from that country. The U.S. pipe was selected to represent typical domestic pipe, specified for use in Government contracts. In price, U.S. pipe falls in the mid-range between Korean and Australian pipe. Korean pipe was selected because it is the least expensive on today's market and therefore the logical choice for large housing tracts. Australian pipe was selected because local dealers indicated it would be of the highest quality.

Initially, a series of samples of these three types was tested via ASTM methods to determine zinc coating thickness and uniformity. Specifications for ASTM A-120 pipe include a minimum weight of coating and state that the coating should be "free of excessive roughness". ASTM A-90, the "weight of coating" test and ASTM A-239, the "Preece test", were utilized in these evaluations. In addition, visual and photographic comparisons of the three types were made.

At the same time, cross sectional pieces of the three types of pipe were examined via scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) to evaluate the physical structure and chemical composition of the zinc coatings. This work was carried out by Hi Rel Metallurgical Laboratories located in Monrovia, California. Subsequently, more detailed work in this area was carried out by Dr. Jerry Thomas and Dr. Ray Lewis, both of U.C. Berkeley, California. Additional samples of Korean, Australian, and U.S. pipes were evaluated for base metal (steel) chemical composition, pipe weld anomalies, and zinc coating structure and appearance. Techniques included SEM, EDX, and emission spectroscopy.

## BENCH STUDIES

The second level of work focused on two possible contributing factors to pitting corrosion, pipe surface anomalies and potential reversal between the iron and zinc layers of the pipe. Two bench-scale set ups were used. For the first, a large constant temperature bath was established at 60°C. A series of glass pans containing aerated solutions of copper, copper plus citrate, and ordinary tap water were immersed in the bath. Replicate samples of pipe having artificially induced surface anomalies were then placed in each of the solutions. Surface anomalies were produced by either drilling into the pipe surface or acid etching a small portion of the pipe surface. Three separate tests were run with this bench test set up, each lasting one to two months. After removal, the pipes were analyzed photographically and via pit depth measurements.

The second bench test followed up on various researchers' observations that under certain conditions pitting of galvanized steel can be caused by potential reversal between the iron and zinc layers. Whereas the zinc in a zinc-iron couple will normally have a potential of about 250 to 300 millivolts (mv) lower than iron, in hot, oxygenated water with appropriate water quality, the zinc can become cathodic to the iron with the latter demonstrating accelerated corrosion. Local waters (well water, Colorado River water, and State water project water) were tested for their tendencies to cause such a potential reversal. The zinc-iron couple consisted of a strip of zinc ribbon and a split section of black iron pipe. Both metals were immersed in a 1500 ml beaker of heated test water, and alternately connected to a potentiometer. A silver/silver chloride electrode was used as a reference, and the voltage changes of the two metals were recorded over time.

## PILOT PLANT STUDIES

The pilot plant was designed and constructed during 1981, and was operated between February 1982 and February 1984. The plant was designed to simulate household operations; influent water flowed through a water heater and the test pipes on a schedule of 10 minutes on, 50 minutes off, for 15 hours, followed by nine hours of no flow. Within this framework, five variables were tested: copper dose, pipe type, mode of pipe exposure to the test water, water quality, and the use of citrated copper. Phase 1 extended for the entire duration of the pilot plant operations, i.e. February 1982 - February 1984. During Phase 1, Colorado River water and six doses of copper: (0, 0.05, 0.10, 0.5, 1.0, and 5.0 mg/L) were tested. For each dose, six lengths of test pipe were exposed, two Korean, two Australian, and two U.S. The "mode of exposure" variable refers to static versus flowing exposure of the pipes to the test solutions. For the static test, one pair of pipes was initially filled with test solution at each copper dose and was held with no flow for a month. This simulated a condition wherein a tract of new houses would be built but not sold right away. The water utilized during plumber's leak testing of the pipes would thus simply remain in the pipes until occupancy.

Phase 2 overlapped with Phase 1, beginning in August 1983 and ending in February 1984. It provided for consideration of the fourth and fifth variables, water quality and citrated copper. To do this, half of the Phase 1 system was shut down, the test pipes replaced, and the influent water changed to SWP water. Copper doses tested were: 0, 5.0 mg/L and 5.0 mg/L plus 2.5 mg/L citrate. Again, six test pipes were set up for each dose and half of each set of six initially received static exposure

to the test solutions. Unlike Phase 1, however, this exposure occurred over a three month rather than a one month period.

Water quality analyses were carried out throughout the pilot plant operation to ensure proper chemical feed and to track any water quality changes occurring within the pilot plant. During both phases, test pipes were periodically removed for analysis. Segments of each pipe were stripped of corrosion product in an inhibited sulfamic acid solution. Pre and post stripped weights recorded the total amount of scale build-up, while analysis of the stripping solution quantified the calcium, zinc, copper, and iron in the scale. X-ray fluorescence measurements of zinc and iron exposed on stripped segments then provided a measure of zinc lost through corrosion. Dr. Jerry Thomas at U.C. Berkeley was also given samples of exposed pipe after they had been in the system for 14 months. He and Dr. Ray analyzed the scale via SEM and EDX.



## SECTION 3

### PIPE STRUCTURE AND MANUFACTURE

Since pipe characteristics were one potential cause of observed pipe failures, part of this project consisted of investigating pipe production processes, checking applicable standards, and then testing various types of ASTM A-120 galvanized pipe (foreign and domestic) to determine if they complied with standards. Within this context, the literature on iron and steel making, pipe production and galvanizing was reviewed, and a tour was made of the Bethlehem Steel Plant in Sparrows Point, Maryland. Applicable ASTM specifications for ASTM A120 pipe were also reviewed, and samples of domestic and foreign pipe from local pipeyards were subjected to tests described within the specifications. Finally, detailed investigations of the physical microstructure and chemical composition of the base metal and of the zinc coating of additional samples were made. Results of these investigations are described below.

#### PIPE MANUFACTURE

Galvanized steel pipe is the product of a series of processes beginning with iron and steel making and including the forming of ingots, roughing the ingots into slabs, reducing the slabs into thin sheets of skelp, rolling and fusing skelp into welded pipe, and finally galvanizing. Figure 2 outlines the basic steps involved. As discussed below, a number of variables enter into these processes, including the type of furnace, the quality of raw materials, and the temperatures in the furnaces and the forming procedures. Manipulation of these variables will dictate the type and quality of steel produced.

The basic raw materials for iron making are iron ore, limestone, and coal. The ore is beneficiated or purified from rock having an initial iron content of around 30 percent to pellets with 80 to 90 percent iron. Iron fines produced during the ore beneficiation are mixed with powdered coal and fused into a cake. The cake is then broken into pieces (termed "sinter") for additional feed to the blast furnace. At times, scrap and mill scale may also be used as part of the iron charge to the blast furnace. Limestone is quarried and crushed into pieces for direct use as a fluxing agent in the blast furnace. A portion of the limestone is converted to lime in high temperature kilns and utilized as a faster acting flux. Coal is cleaned of some impurities via froth flotation or cyclone methods and then baked to produce the coke which is the actual fuel utilized in the blast furnaces. In the coke ovens, much of the volatile material in coal is burned off and the exhaust directed to various recycling processes. The coke thus produced for blast furnaces burns cleanly and does not leave any residual sticky mass within the furnaces.

In operating the blast furnace, purified iron ore, lime, limestone, and coke are charged into the top of the furnace. Hot air is blown in at the bottom to instigate the heating and reactions within the stack. As the ore, limestone and coke sink through the stack they become hotter and hotter. About halfway down, the limestone begins

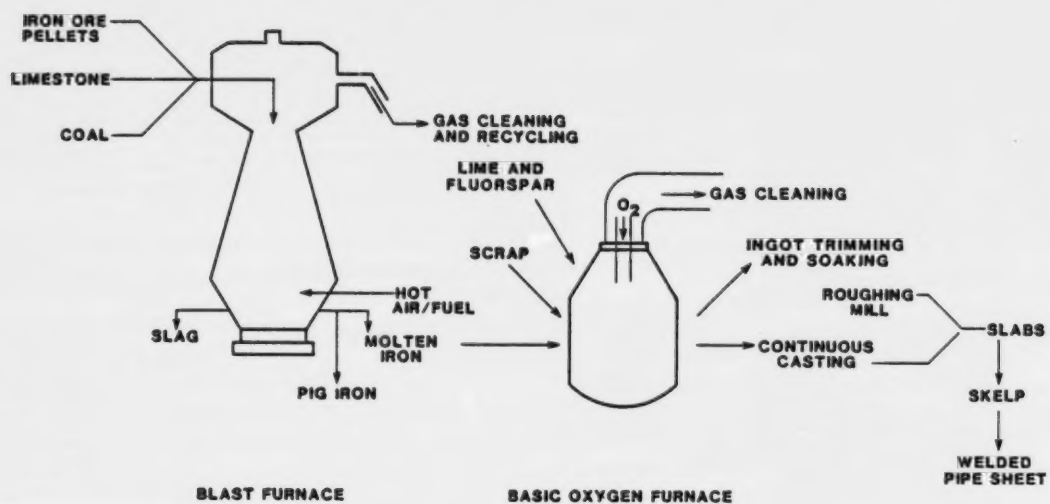


Figure 2. Basic processes for transforming iron ore into welded steel pipe.



reacting with impurities in the ore and coke to form a slag. At the bottom of the furnace, where temperatures are over 3000°F, molten slag floats on a pool of molten iron. The slag is drained off the top and the liquid iron from the lower tap hole. At this point, the metal is about 93 percent iron and seven percent extraneous elements. Most of the iron is transported via hot metal cars to the steel making facilities. Some is poured directly into molds for cooling and transport to customers. This latter product is termed "pig iron".

Steel is basically iron plus a small amount of carbon (generally less than one percent). Three types of furnaces are used to make steel: the basic oxygen furnace, the electric furnace, and the open hearth furnace. Currently, the basic oxygen furnace dominates U.S. production. Molten iron, scrap, lime, fluorspar, and oxygen are the primary raw materials. In addition, about 30 other alloying elements are utilized to produce steels of specified properties such as high temperature tolerance, corrosion resistance, tolerance to bending and forming, hardness, etc. These alloying elements include manganese, nickel, chromium, tin, silicon, molybdenum, titanium, etc. Most are imported to the U.S. from various countries around the world.

In the basic oxygen furnace, scrap and molten iron are charged into the furnace shell and an oxygen lance is lowered to sit above the metal and begin the ignition process. Lime, fluorspar, and sometimes scale are then added. The lime and fluorspar combine with impurities to produce a floating slag layer on top of the molten steel. Periodically, the oxygen is shut off, the temperature and sometimes carbon content of the metal are tested, and selected alloys are added.

Following the furnace, the steel is poured into ingot molds or into a strand casting machine for solidification. For steel intended to produce welded pipe and tubing, the cooled ingots are put through a roughing mill to produce rectangular steel sections called slabs. In the more modern, continuous casting process molten steel is formed directly into the slabs bypassing ingot formation, soaking and cooling, and roughing.

The slabs are sent to the hot strip mill to be rolled into continuous thin ribbons called skelp. The skelp is formed into the proper width and thickness to roll directly into pipe. Figure 3 illustrates the formation of pipe from skelp via the continuous butt weld and the electric resistance weld processes. For butt welding, the skelp is fed continuously through a furnace where the two edges are rolled up, heated and fused together. The temperature is high enough to meld the edges together. In an electric resistance tubing mill, the process begins much like that in a continuous butt weld mill, without the skelp heating furnace. Instead the pipe is joined by an electric resistance weld. Neither process incorporates new materials into the pipe; both welds are formed from the pipe steel itself. In the U.S. and Australia, butt welding is utilized; in Korea, electric resistance welding is employed.

After welding, the pipe is cooled and sent to the galvanizing shop. There the pipe is first dipped as a loose bundle into an acid pickling bath. The bundle is rolled around to obtain good exposure, followed by rinsing and a pre-flux dip consisting of zinc and ammonium chloride. The pipe is then fed in individual pieces into the zinc galvanizing bath, and pulled out individually into an annealing furnace. Immediately after the furnace, the pipe passes through a compressed air ring where hot steam is blown around the outside and through the inside of the pipe to rid the surface of excess zinc. After steaming, the pipe is cooled and rolled down a ramp onto a platform where it is inspected at both ends. The next step is a chrome dip to give a final seal to the pipe.

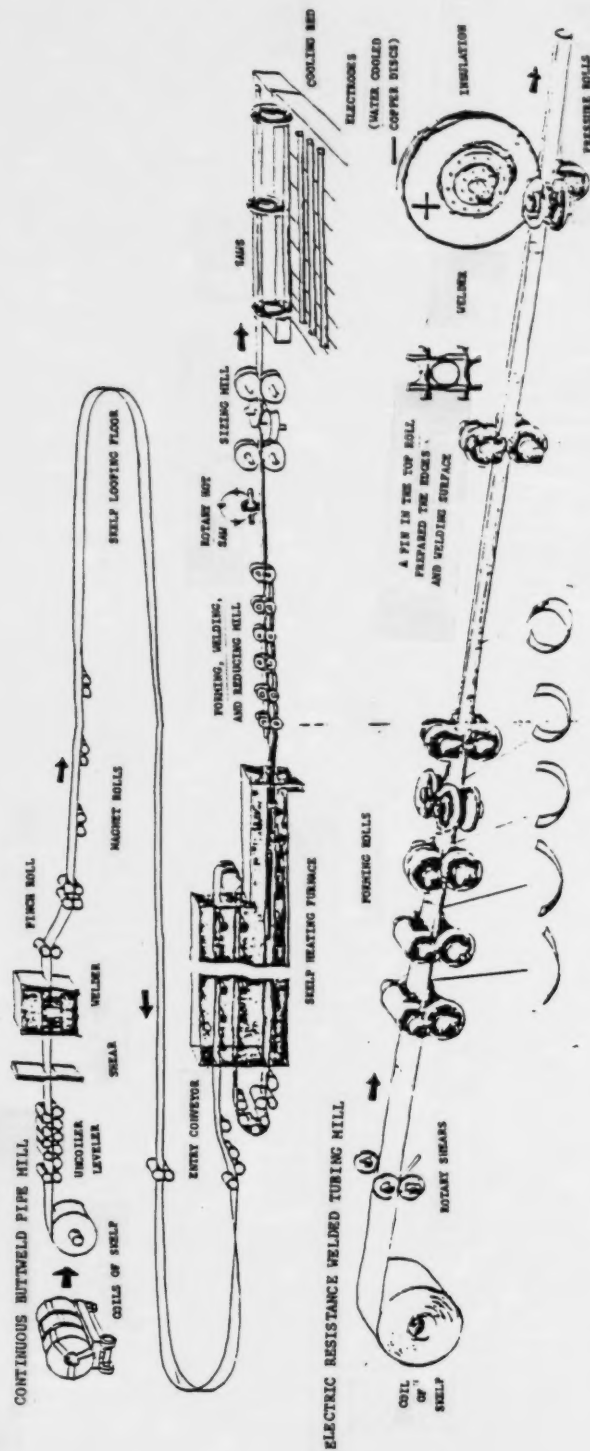


Figure 3. The essential elements of pipe making.

The chrome layer is intended to coat the pipe at 4 micrograms per square inch. The final step in the galvanizing is to stamp the I.D. of the plant on the pipe.

Variations in the above procedures can occur. Sometimes the skelp used to form the pipe is cut too wide to form the correct size pipe and the excess width is forced into the weld, creating a visible bead. Variations in the smoothness of the inside zinc coating sometimes occur when the steam blowing step is delayed too long and some of the zinc begins to harden, or when the steam is at an inappropriate temperature or pressure. Air has been substituted for steam in some overseas locations, and lacquer has sometimes been used instead of chrome, depending on their relative costs. If lacquer is used, it is painted on the outside of the pipe only. Chrome, on the other hand, is applied as a dip which coats both the inside and the outside of the pipe. If the chrome dip is too concentrated, it will give the pipe a yellowish hue. If the galvanizing coat is too thin, a dull appearance may result. If the pipe spends too much time in the hot dip or the temperature is too high, an alloy will develop which does not have the same protective properties as a proper hot dip zinc coating.

#### TESTING SPECIFICATIONS

Three ASTM specifications outline requirements which apply to galvanized pipe for "ordinary uses" such as steam, water, gas and air lines; ASTM A120-82 characterizes the pipe itself, ASTM AB6-77 characterizes the slab zinc utilized in the galvanizing process, and ASTM A385-80 outlines recommended practices for galvanizing. ASTM A120 specifies continuous butt-welding for pipe under 4-inches in diameter, unless otherwise required, and electric-welding for pipe over 4-inches in diameter. The pipe must be coated with zinc inside and outside by the hot dip process. The resultant weight of the zinc coating (inside plus outside) must not be less than 1.8 ounces per square foot (0.55 kilogram per meter<sup>2</sup>) as determined from the average result of two, 4-inch specimens removed from either end of one length of pipe. In addition, the zinc coating weight of either of the two specimens taken for testing must not be less than 1.6 ounces per square foot (0.49 kilogram per meter square).

ASTM A120 also specifies a hydrostatic test for the sizes commonly used in consumer plumbing; the test pressure is 700 psi (4.83 MPa). Finally, the pipe must be reasonably straight and free of defects while the zinc coating must be "free of voids or excessive roughness".

ASTM A120 does not include any requirements for the chemical composition of the pipe. Other steel products require a relatively precise chemical makeup to allow for specific applications such as high heat, bending, etc. For example, the specification ASTM A53 covers black and hot-dipped, zinc-coated (galvanized), welded and seamless steel pipe in nominal sizes from 1/8-inch to 26-inches inclusive, and which is suitable for coiling, bending, and flanging, subject to certain qualifications. Steel for this type of pipe must conform to the chemical requirements shown in Table 5. ASTM A120 on the other hand, is not intended for close coiling or bending or for high temperature service. Thus, no chemical limits are specified for the steel in this type of pipe and greater quality variation occurs.

The zinc utilized in the galvanizing can be any of three grades described in ASTM B6: special high grade, high grade or prime western. Each has a specified maximum level for lead, iron, cadmium, and aluminum and a minimum level of zinc (by difference). Prime western, which is normally used in the manufacture of galvanized

TABLE 5  
CHEMICAL REQUIREMENTS OF STEEL FOR  
ASTM A-53 PIPE

| Composition, Maximum %                            |               |                  |                   |               |
|---------------------------------------------------|---------------|------------------|-------------------|---------------|
|                                                   | <u>Carbon</u> | <u>Manganese</u> | <u>Phosphorus</u> | <u>Sulfur</u> |
| Type S (seamless pipe)                            |               |                  |                   |               |
| Open-hearth, electric-furnace<br>or basic-oxygen: |               |                  |                   |               |
| Grade A                                           | 0.25          | 0.95             | 0.05              | 0.06          |
| Grade B                                           | 0.30          | 1.20             | 0.05              | 0.06          |
| Type E (electric-resistance-welded)               |               |                  |                   |               |
| Open-hearth, electric-furnace<br>or basic-oxygen: |               |                  |                   |               |
| Grade A                                           | 0.25          | 0.95             | 0.05              | 0.06          |
| Grade B                                           | 0.30          | 1.20             | 0.05              | 0.06          |
| Type F (furnace-welded pipe)                      |               |                  |                   |               |
| Open-hearth, electric-furnace<br>or basic oxygen  |               |                  | 0.08              | 0.06          |



pipe for domestic plumbing, has limits of 1.4 percent, 0.05 percent, 0.2 percent and 0.05 percent for lead, iron, cadmium, and aluminum, respectively.

ASTM A385 describes the structure and metallurgy of a normal hot-dip zinc coating, suggesting the presence of five separate metallurgical layers; (1) the base steel, (2) the gamma layer at the steel coating interface, (3) the delta layer which is iron rich zinc, (4) the zeta layer which can be characterized as the iron/zinc diffusion zone, and (5) the eta layer which is virtually pure zinc in composition. Impurities such as lead and cadmium are generally found at their highest concentrations in the eta layer. A typical cross-section showing these layers is shown in Figure 4. ASTM A385 also makes note of the need for steel meeting certain chemical requirements. Specifically, levels of carbon, phosphorus, manganese, and silicon above 0.25 percent, 0.05 percent, 1.3 percent, and 0.05 percent, respectively in the base steel may result in coatings different from those normally encountered. Often such impurities result in a more brittle and less adherent coating with a dull or mottled appearance. Microscopic examination will show a dominance of the zeta layer and a greatly reduced or eliminated eta layer, the result of accelerated growth of the compound layers.

The quality of the galvanized pipe coating is normally evaluated under two different ASTM test specifications; (1) ASTM A90-81 characterizes the weight of the zinc coating, and (2) ASTM A239-73, the Preece Test, evaluates the uniformity of the coating. ASTM E376-69 is an alternate procedure for testing coating thickness via magnetic and eddy current-type devices, but is not in common use. In ASTM A90, the coating is evaluated by weighing a specimen, stripping the zinc coating with a hydrochloric acid-antimony trichloride solution and reweighing the specimen. The weight of the coating is determined by difference. The Preece Test, ASTM A239, employs repeated exposure of the coated surface to a saturated copper sulfate solution until an area of the base metal of 0.077 centimeters<sup>2</sup> or larger is exposed. Normally the base metal is easily recognized because ferrous metals will cause a bright, adherent copper deposit on these areas, whereas the surrounding zinc will not.

Two other ASTM specifications refer to the "stout knife test" to determine adherence of the hot dip zinc coating to the base metal. Both ASTM A 153-82 (Zinc Coating on Iron and Steel Hardware) and ASTM A 123-78 (Zinc Coatings on Products Fabricated from Rolled, Pressed and Forged Steel Shapes, Plates, Bars and Strip) specify that the adherence of the zinc coating to the surface of the base metal shall be determined by cutting or prying with the point of a stout knife, applied in a manner tending to remove a portion of the coating. If the coating flakes off as a layer and exposes the base metal, the adherence is considered inadequate.

#### TYPE AND VARIABILITY

To determine the actual characteristics of ASTM A120 pipe as supplied by local Los Angeles dealers, samples of three types of pipe (U.S., Australian, and Korean) were obtained from area pipeyards. The U.S. pipe was selected because it is specified for use in government contracts. In price, U.S. pipe falls in the mid-range between Korean and Australian pipe. Korean pipe was selected because it is the cheapest on the market and therefore the logical choice for large housing tracts. Australian pipe was selected because local dealers indicated it is of the highest quality. The pipe was purchased as it would be by a local contractor, i.e. in 21 foot lengths. Each length was cut into seven, 3 foot sections and one section was then split open longitudinally for examination.



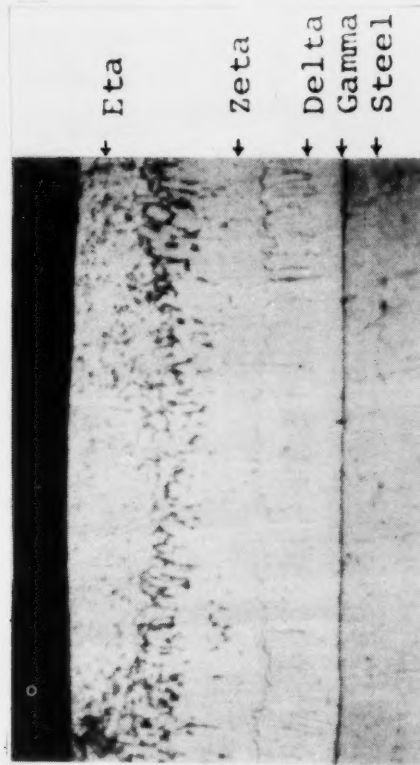


Figure 4. Photomicrograph of normal galvanized coating (X400)

The surface differences among the three sources was quite distinctive. Figures 5a, b, and c show the differences seen among the three types. While the Australian pipe appears relatively smooth and uniform, the Korean pipe contains distinctive, intermittent blemishes and shows a clear ridge along the weld. A few spots on the Korean pipe show rust. The U.S. pipe shows the most surface variability, with zinc coating colors ranging from shiny silver-gray, to yellowish silvery-gray, to dark blue and black. Several pieces contain a series of wave-like ridges.

These surface characteristics were observed along the total length of individual pieces of pipe; i.e. each Australian pipe was smooth and uniform, each Korean pipe was generally smooth with isolated blemishes, and each U.S. pipe showed color and texture variations along its entire length. These observations suggested that the Korean and U.S. pipes might be more susceptible to pitting-type corrosion.

Because the differences in the surface quality of the three types of pipe might reflect the overall quality of their galvanizing, the coating thickness tests described earlier were conducted on several pipe samples.

In conducting these tests, seven, 21 foot lengths of each of the three types of pipe were used. Three samples were cut from one end and three from the middle of each length. Figure 6 identifies the tests conducted on each sample section. Both a one-sided (inside) and a two-sided thickness test were conducted to see if a difference between the inside and the outside coating thicknesses could be observed. The Preece test was conducted for both the inside and outside coats simultaneously. Figure 7 presents the results of the two-sided coating thickness test. As shown, all the Australian pipe met the 1.8 ounce per square foot specification for coating thickness and all 14 samples fell within a fairly narrow range of coating thickness. The U.S. pipes met the specification, but the range of coating thicknesses was highly variable. To a large degree, this results from large ridges or deposits of excess zinc which occurred on a number of U.S. pipes. This extra zinc resulted in very high apparent weights; in one case the calculated weight of coating was 5.9 ounces per square foot. The Korean pipes were more uniform than the U.S. pipes, but 11 of the 14 samples did not meet the weight specification.

The single-sided weight of coating test indicated that the inside coating of zinc may be slightly heavier than the outside for all three types of pipe, however, insufficient data were available for statistical confirmation. If true, this would be beneficial from the standpoint of internal, uniform corrosion.

The results of the Preece test reiterate the pattern observed in the thickness test. As Figure 8 shows, the Australian and Korean pipes have relatively uniform coating thicknesses, while the U.S. pipe is decidedly non-uniform. However, the U.S. pipe non-uniformity is skewed in the direction of greater coating weight. Of the 14 samples tested, 13 required more than one, one-minute dip to break through the zinc coating. This contrasts with the Korean pipe where only two out of the 14 samples required more than a single dip. The Australian pipe again performed well; the majority of samples required two dips, four required only one dip, and two required three dips.

Based on the examination of the surface characteristics of the three types of pipe, and on the analyses of coating thickness and uniformity, some general observations can be made:

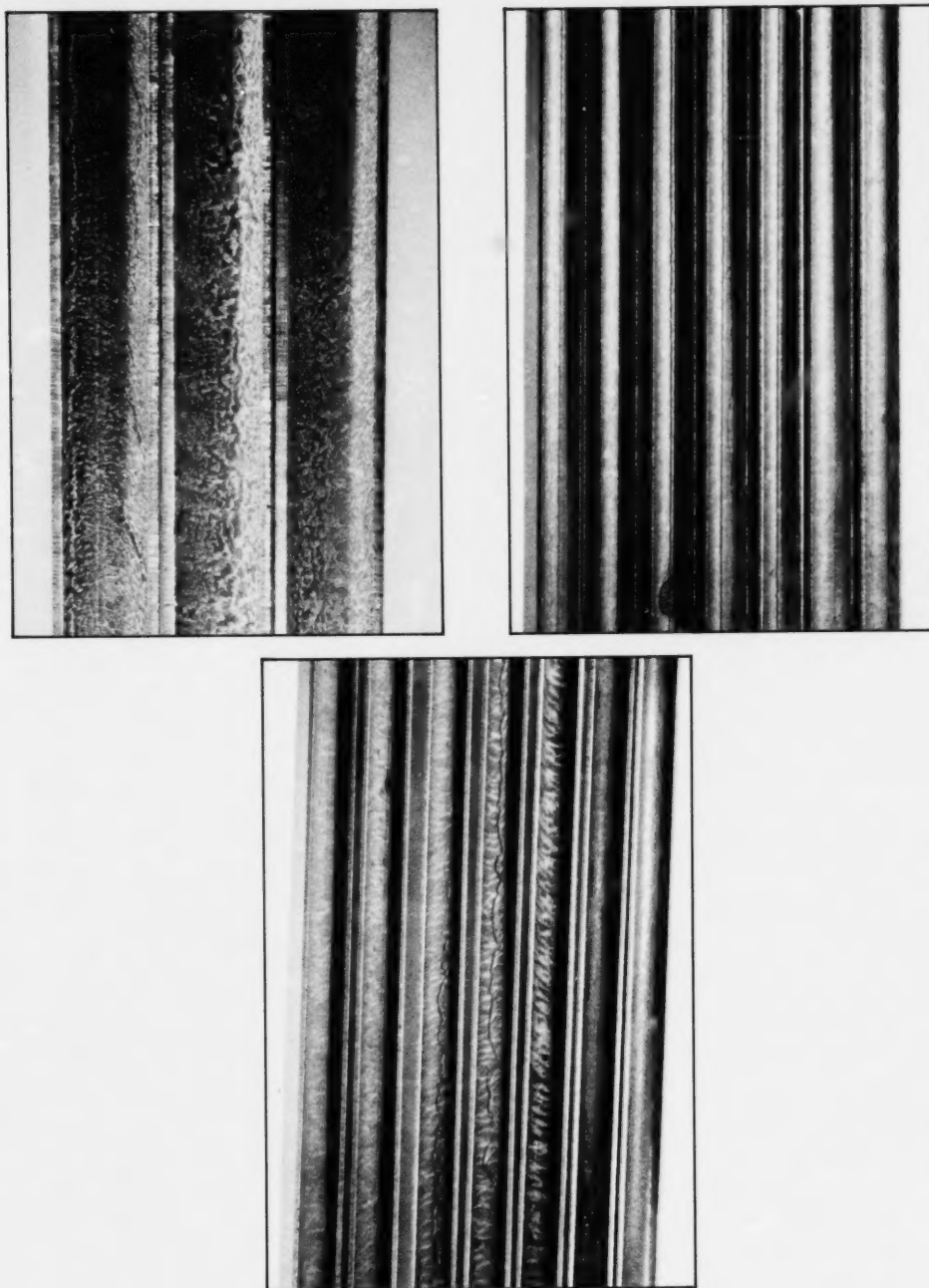


Figure 5. Sections cut from individual pieces of Australian, Korean, and U.S. pipe. Clockwise from upper left: Australian pipe, Korean pipe, and U.S. pipe.

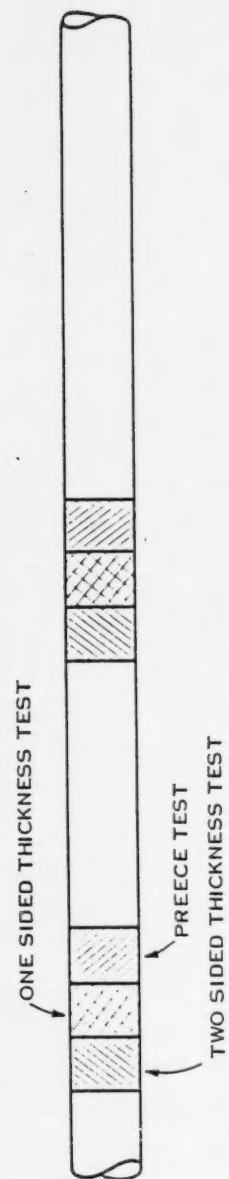
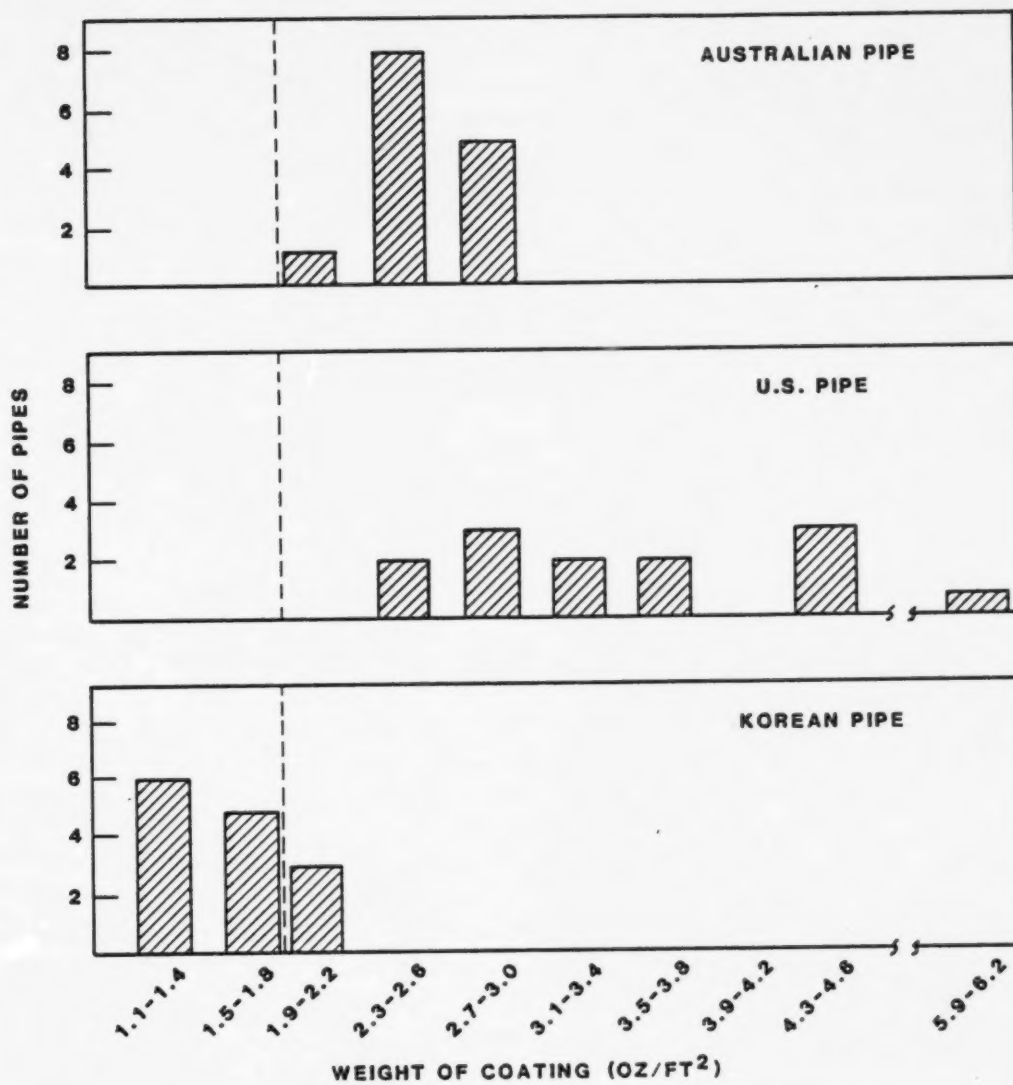


Figure 6. Test locations on U.S., Australian, and Korean pipe.



----- INDICATES MINIMUM ASTM COATING WEIGHT

Figure 7. Two-sided coating thickness test.



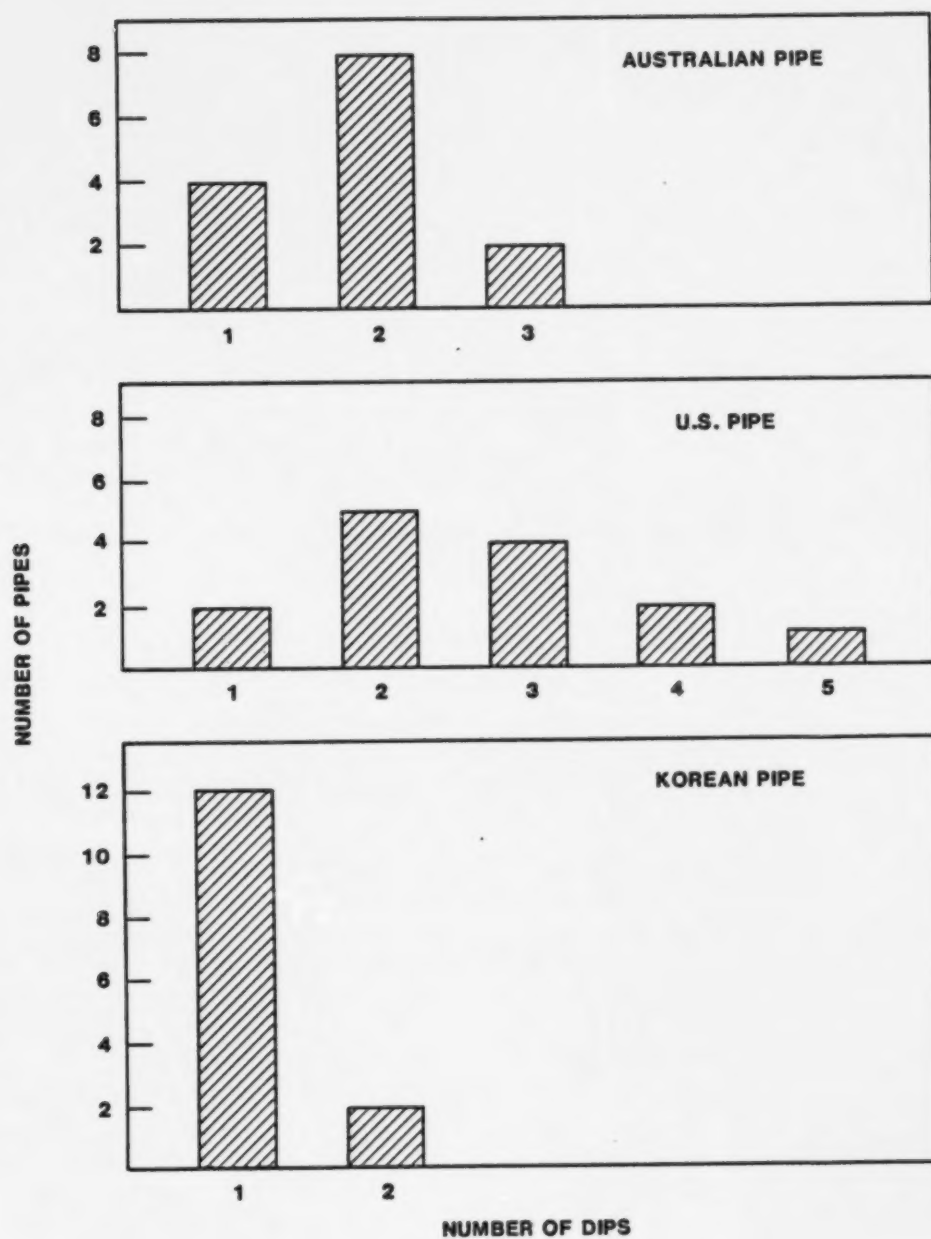


Figure 8. Preece test for locating the thinnest spot in galvanized coat.

1. Australian pipe - the zinc coating meets the thickness specifications and is uniformly smooth.
2. U.S. pipe - the coating meets thickness specifications but shows substantial zinc layer heterogeneity.
3. Korean pipe - Most of the coating is below specifications and shows intermittent surface anomalies.

These tests and observations have been made for a single source for each pipe type. Thus, another U.S. or Korean producer of ASTM A120 pipe, for example, might have a better product than that observed in this experiment.

#### ZINC COATING MICROSTRUCTURE - PRELIMINARY TESTS

Along with the ASTM testing for coating thickness and uniformity, some preliminary testing of the coating structure of Australian, Korean, and U.S. pipes was carried out by Hi-Rel Metallurgical Laboratories in Monrovia, California. The intent was to ascertain if the coatings matched the structures identified in ASTM A385-80 (Figure 4).

Samples of the three types of pipe were cut in cross section, mounted in epoxy, and etched for (1) scanning electron microscopy (SEM) determination of the various alloy layers, (2) visual measurement of the total zinc coating thickness, and (3) energy dispersive X-ray (EDX) analysis of the elemental composition of the layers.

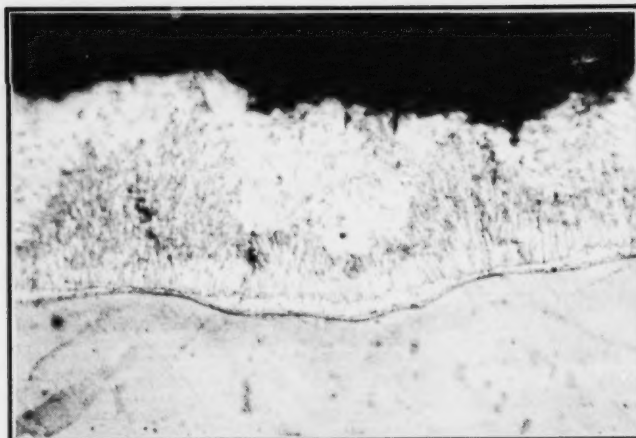
Figure 9a, b, and c show the coating structure observed for the three samples via SEM at 425X. All three have the five layers of a typical coating; base steel, gamma interface, delta, and zeta alloy layers and an essentially pure zinc eta layer.

The Hi-Rel lab then analyzed the delta, zeta, and eta layer thicknesses and elemental compositions. Table 6 presents the average thicknesses of the total zinc coating and of the delta, zeta, and eta layers for each sample. As shown, the Korean pipe has the thinnest overall coating and the U.S. the thickest. This agrees with the "weight of coating" tests described in the previous section.

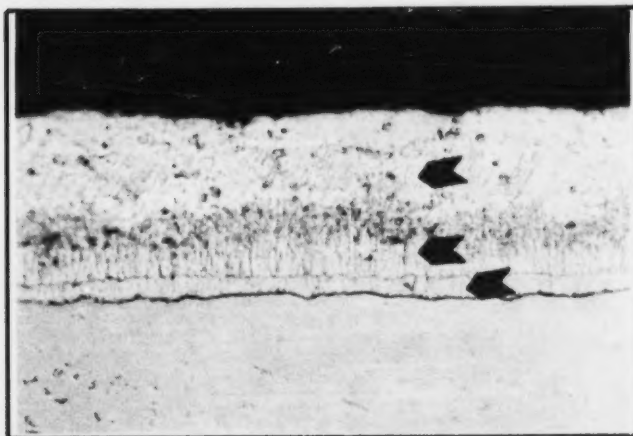
The EDX results, presented in Table 7, show no abnormal components in any of the three layers. A small amount of lead showed up in the zinc (eta) layer of the U.S. pipe, however ASTM B-6, the specification for zinc used in galvanizing, permits prime western zinc, typically used for ASTM A120 pipe, to contain up to 1.4 percent lead.

#### ZINC COATING AND BASE METAL MICROSTRUCTURES - IN-DEPTH TESTS

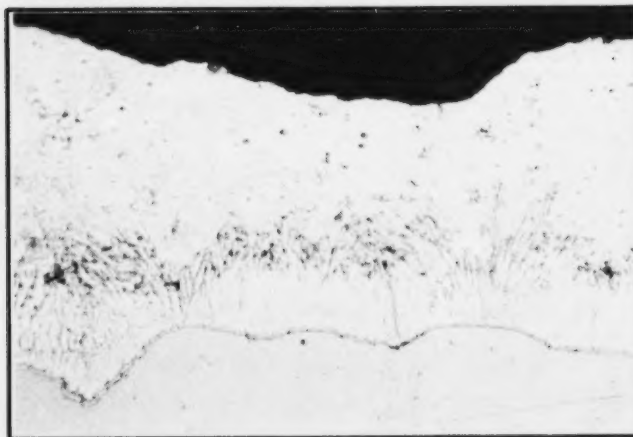
Following the Hi-Rel work, a more in-depth study by Dr. Jerome F. Thomas of U.C. Berkeley was commissioned. Dr. Thomas examined anomalies in the structure and chemical composition of the base steel and of the zinc coating of the three makes of galvanized steel pipe. (In a second phase of work discussed in Chapter 5, Dr. Thomas also examined the corrosion products on pipes taken from the pilot plant after 14 months of exposure). Results of his tests on new pipe are described below.



AUSTRALIAN



KOREAN



U.S.

Figure 9. Iron-zinc interface under high magnification (425X).

TABLE 6  
ZINC COATING THICKNESS MEASUREMENTS<sup>a</sup>  
PIPE INTERIORS

| <u>Area Measured</u> | <u>Pipe Type</u> |                                         |               |
|----------------------|------------------|-----------------------------------------|---------------|
|                      | <u>U.S.</u>      | <u>Australian</u><br>Thickness (Inches) | <u>Korean</u> |
| Total Coating        | 0.0057           | 0.0035                                  | 0.0028        |
| Delta Layer          | 0.00056          | 0.00031                                 | 0.00037       |
| Zeta Layer           | 0.00130          | 0.00183                                 | 0.00123       |
| Eta Layer            | 0.00280          | 0.00160                                 | 0.00145       |

a Calibrated filar eyepiece measurements.  
Average of two measurements.

TABLE 7  
ELEMENTAL COMPOSITION OF PHASES<sup>a</sup>

| <u>Pipe Type</u> | <u>Delta</u> | <u>Zeta</u> | <u>Eta</u>       |
|------------------|--------------|-------------|------------------|
| U.S.             | zinc, iron   | zinc, iron  | zinc, iron, lead |
| Australian       | zinc, iron   | zinc, iron  | zinc             |
| Korean           | zinc, iron   | zinc, iron  | zinc, iron       |

a Based on Energy Dispersive X-ray analysis conducted by Hi-Rel Laboratories (Appendix A).



### Structure and Composition of Base Metal

Chemical analysis of the base metal via emission spectroscopy was carried out in the range 0.020 to 0.025 inches below the surface. Table 8 lists the chemical composition of the steel of Korean, Australian, and U.S. pipe. As shown, the three types of pipe do not differ significantly in the amounts of various trace elements present, however Korean pipe has a lower carbon content than either the Australian or the U.S. pipe. As was noted earlier, ASTM A120 pipe does not have chemical limitations placed upon its chemical content. Thus, the three types of pipe would all appear to be acceptable for use as water lines under these specifications. ASTM A53-83, the specification for galvanized pipe which can be welded, coiled, bent and layered, does suggest maximum limits for trace elements in the steel, however, to ensure a high quality adherence of the zinc coating. These limits are as follows:

C - 0.25 percent  
P - 0.05 percent  
Mn - 1.3 percent  
Si - 0.05 percent

When compared with the experimental results of Table 5, each of the three pipe makes falls within these limits.

Figures 10, 11, and 12 show cross sections of new pipe of the three manufacturers. The interior welds seam of the Korean pipe is readily apparent, in contrast to the smooth continuum of the U.S. and Australian pipes. Figure 13 illustrates the etched microstructure of the Korean weld area at 40X magnification. Discontinuities within the seam are apparent. These may serve as sites for initiating corrosion by acting as a trap for acid, caustic, or rinse water during the pre hot-dip processes. The Australian and U.S. pipe were examined for corresponding discontinuities within the steel matrix but none were found.

### Zinc Coating Structure

Figures 14, 15, and 16 are photomicrographs of the zinc coatings of Korean, Australian, and U.S. pipe. The photomicrograph of the Korean pipe shows a possible interface abnormality between the base metal and the zinc-iron alloy. In essence, an apparent discontinuity exists in the adhesion of the hot-dip zinc coating to the base metal. The Australian and U.S. photomicrographs, on the other hand, show a relatively smooth transition from the steel to the iron-zinc alloy layer. Poor adhesion of the hot dip coating to the steel can be an important factor in reducing corrosion resistance.

TABLE 8  
TRACE ELEMENTS FOUND IN BASE METAL  
OF GALVANIZED STEEL PIPE

| Trace<br>Element | Pipe Manufacturer |                   |             |
|------------------|-------------------|-------------------|-------------|
|                  | <u>Korean</u>     | <u>Australian</u> | <u>U.S.</u> |
| C                | .03%              | .12%              | .14%        |
| Mn               | .35%              | .46               | .42         |
| P                | .014              | .029              | .008        |
| S                | .016              | .035              | .020        |
| Si               | .006              | .02               | <.005       |
| Cu               | .02               | .02               | .03         |
| Cr               | .01               | .01               | .05         |
| Ni               | .02               | .01               | .01         |
| Mo               | <.005             | <.005             | .005        |
| Al               | .03               | .007              | <.005       |
| V                | <.005             | <.005             | <.005       |
| B                | <.0005            | <.0005            | <.0005      |
| Fe               |                   | Base              |             |

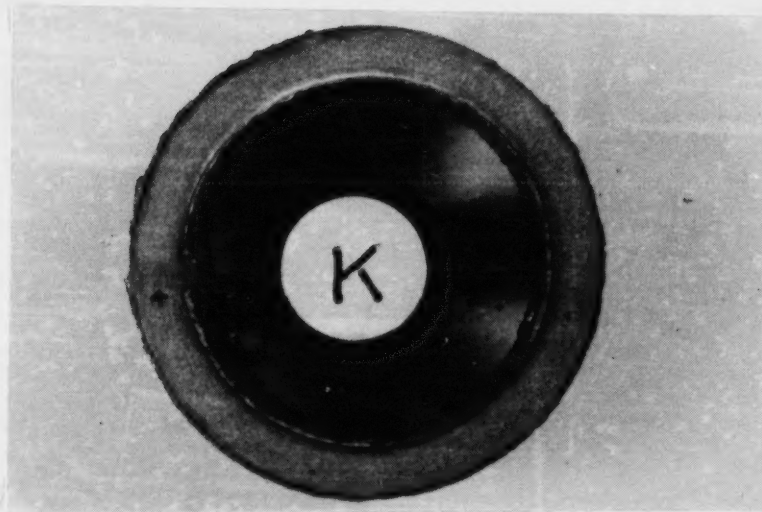


Figure 10. Transverse section of Korean galvanized steel pipe.

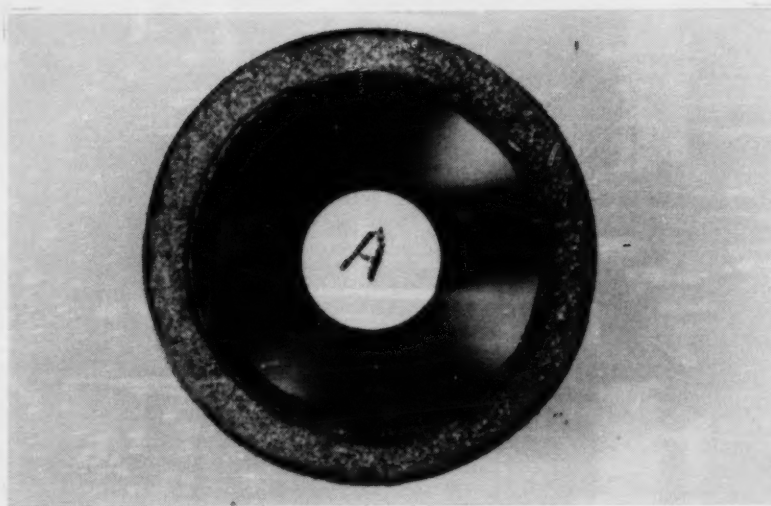


Figure 11. Transverse section of Australian galvanized steel pipe.

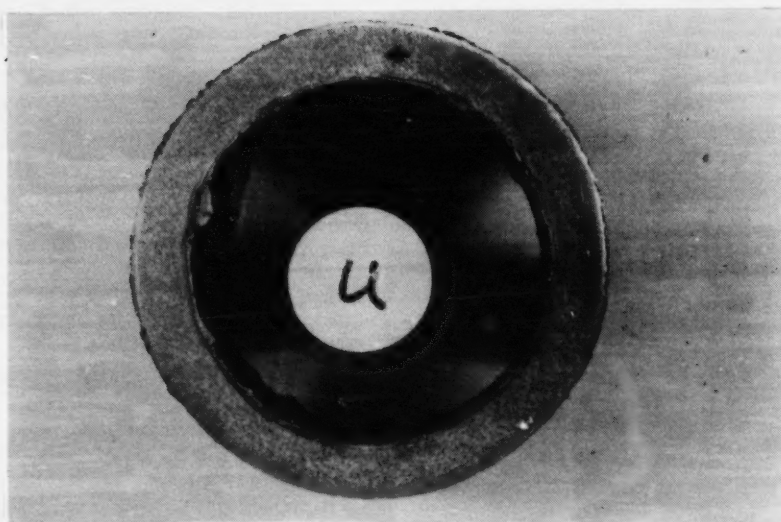


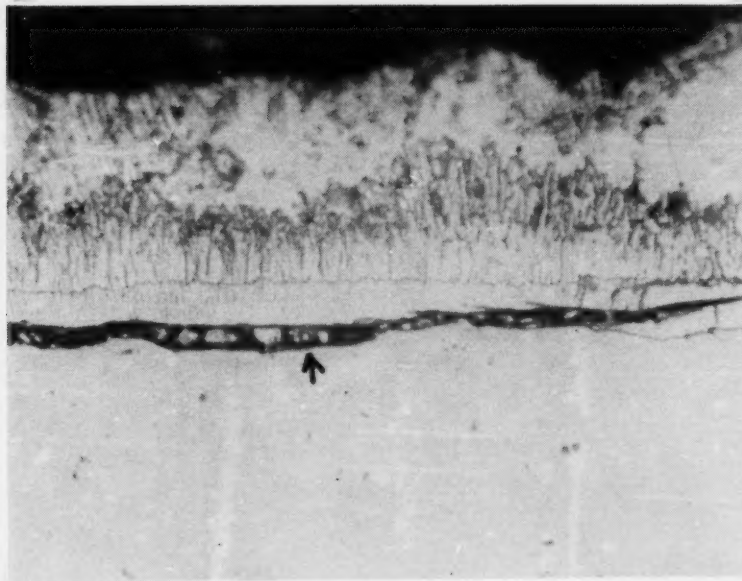
Figure 12. Transverse section of U.S. galvanized steel pipe.





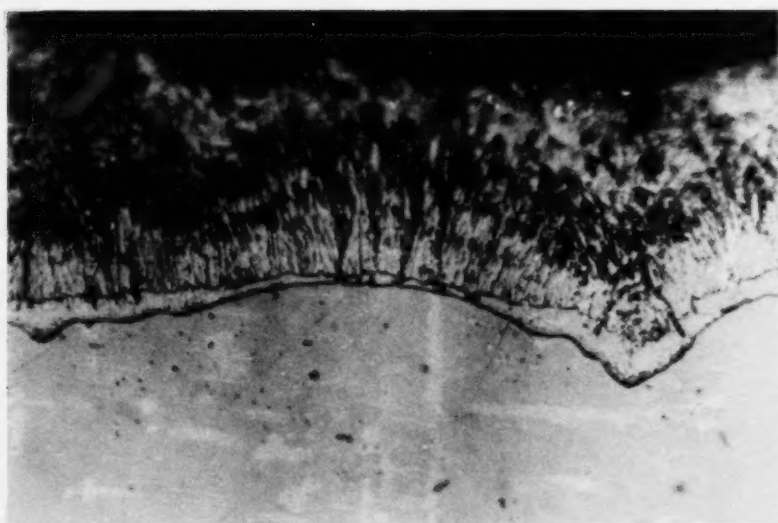
40X

Figure 13. Etched microstructure of weld zone  
of Korean galvanized steel pipe.



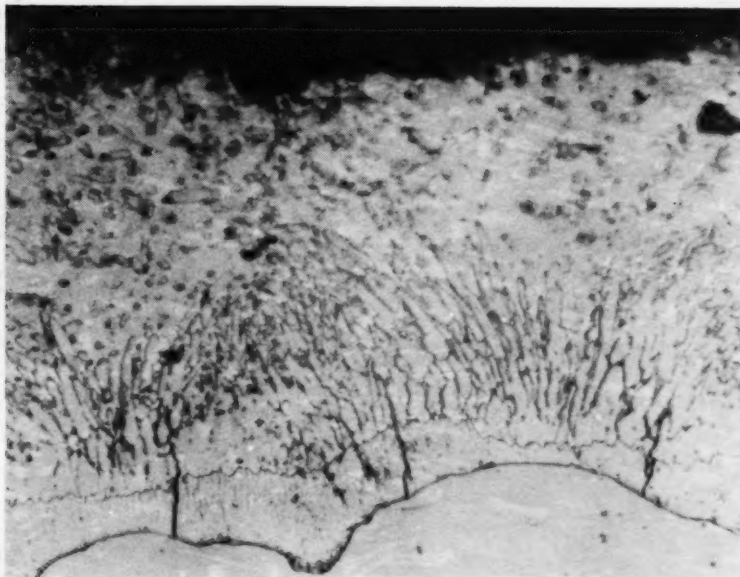
450X

Figure 14. Microstructure of Korean galvanized steel pipe.



450X

Figure 15. Microstructure of Australian galvanized steel pipe.



450X

Figure 16. Microstructure of U.S. galvanized steel pipe.

## SECTION 4

### BENCH STUDIES

Two sets of bench-scale investigations were conducted. The first followed up on observations by various researchers that in certain waters reversal of polarity can occur between zinc and iron. When this happens, the zinc fails to protect the iron (or steel) and rapid corrosion of the latter can occur. The second set of bench studies considered further the role of surface anomalies in accelerating pitting corrosion of galvanized steel pipe. Both sets of studies are described below.

#### POTENTIAL REVERSAL BETWEEN ZINC AND IRON

The use of a thin coating of zinc to protect a steel substrate depends on two attributes of zinc: (1) zinc generally corrodes at a much slower rate than mild steel (one-tenth to one-fortieth the rate) and thus forms a physical barrier between the steel and its (water) environment, and (2) zinc's lower electrode potential makes it corrode preferentially to steel. This sacrificial effect extends even over small breaks or holidays in the zinc layer where the steel is directly exposed to water. Further protection is often afforded at these holidays when zinc corrosion products build up and seal off such breaks.

Under certain conditions, however, premature pitting failure of galvanized pipe has been demonstrated to occur due to potential reversal between the iron and the zinc. Schikorr<sup>(5)</sup> was the first to demonstrate this phenomenon. He noted that the relative potentials of zinc and iron can be reversed at elevated temperatures. He also showed that the reversal is due primarily to an upward shift in the potential of the zinc, while the steel potential shifted only slightly downwards (Figure 17).

After Schikorr, a series of workers analyzed more precisely the conditions under which such reversals might be expected (Gilbert<sup>(6)</sup>; Hoxeng and Prutton<sup>(7)</sup>; Hoxeng<sup>(8)</sup>; Guest<sup>(9)</sup>; Hubbard and Shanahan<sup>(10)</sup>; VonFraunhofer and Lubinski<sup>(11)</sup>; and Ashworth and Fairhurst<sup>(12)</sup>).

Gilbert<sup>(13)</sup> obtained potential reversals at temperatures over 60°C in oxygenated, hard tap water. He also obtained reversal in hot distilled water, but not consistently. By adding different ions to the distilled water however, he observed that bicarbonate encourages reversal while chloride and sulfate discouraged reversal. Hoxeng<sup>(7)</sup> continued to work with synthetic water solutions and found that nitrate also encouraged reversal while silicates and calcium made the zinc more anodic.

Figure 18 demonstrates the importance of temperature and bicarbonate concentration in achieving potential reversal. As shown, in a distilled water solution containing 15 ppm  $\text{HCO}_3$ , no reversal was obtained, while with 115 to 140 ppm  $\text{HCO}_3$  reversal occurred at  $T < 30^\circ\text{C}$ . Figure 19 shows the stabilizing effect of silica and calcium.



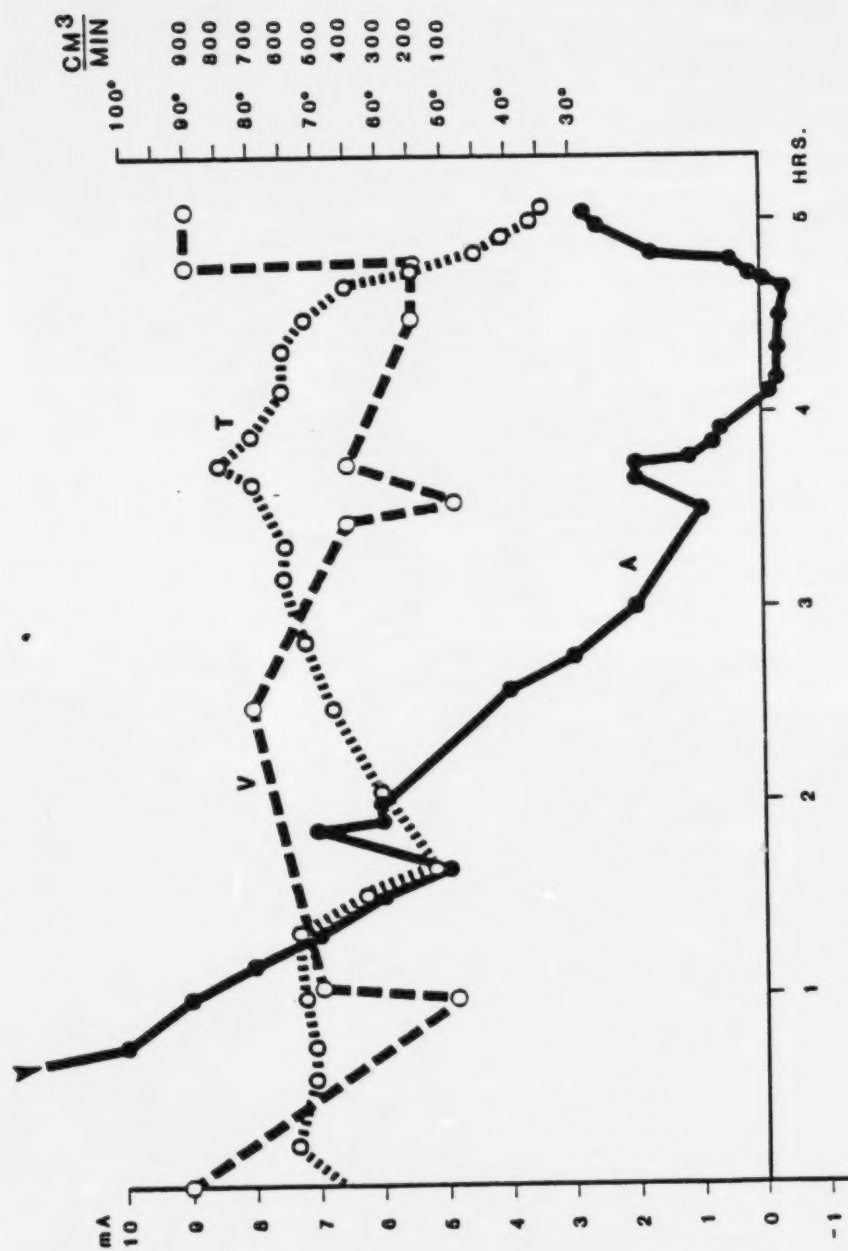
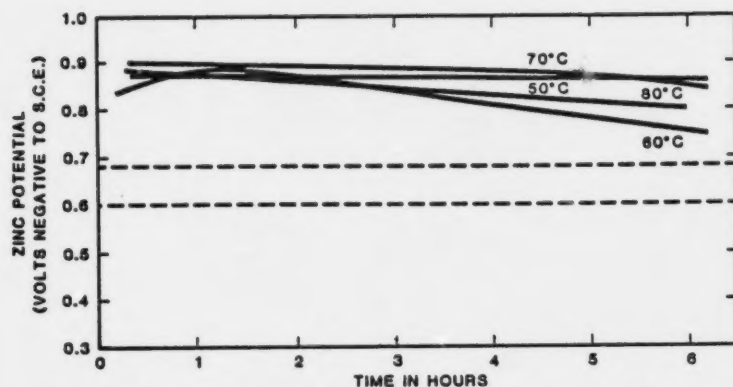
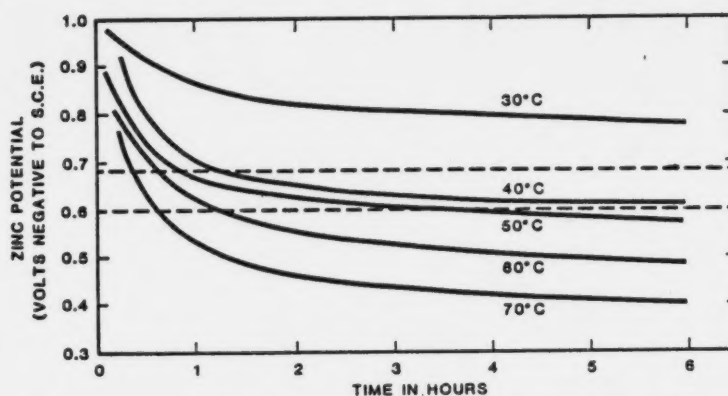


Figure 17. Schikorr's experiment with iron vs. zinc in hot tap water current(A), Temperature(T) and velocity(V).



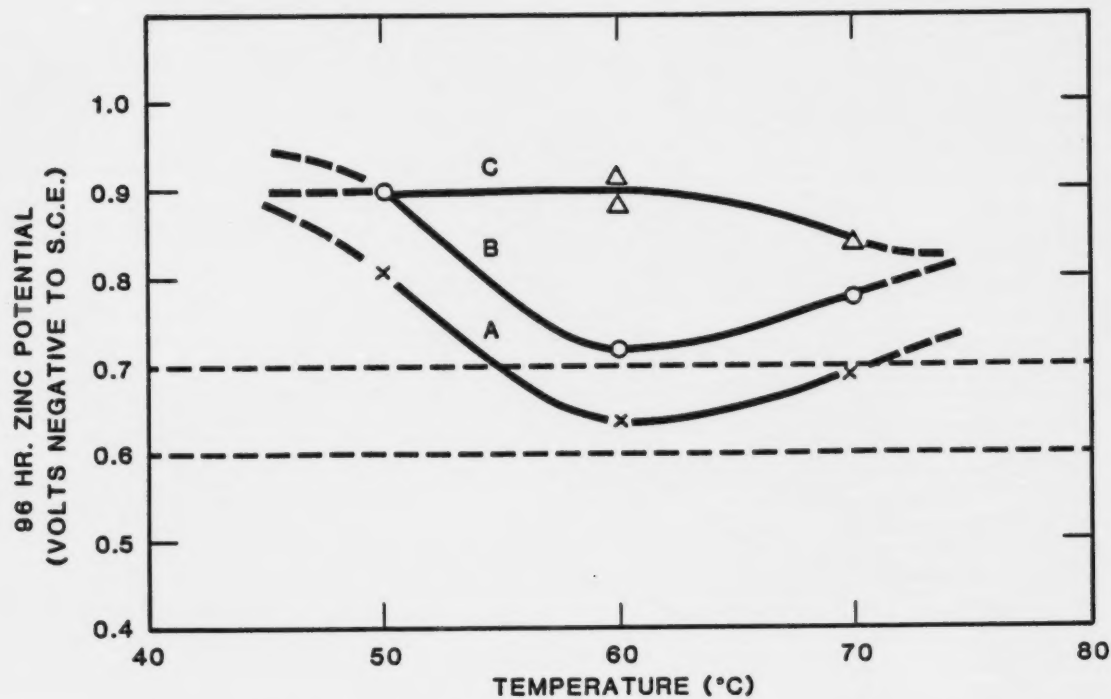
SOLUTION COMPOSITION: 15 PPM  $\text{HCO}_3^-$ , 10 PPM  $\text{SO}_4$ , AND 10 PPM  $\text{NO}_3^-$  (SODIUM SALTS ADDED TO DISTILLED WATER).



SOLUTION COMPOSITION: 115-140 PPM  $\text{HCO}_3^-$ , 10 PPM  $\text{SO}_4$ , AND 10 PPM  $\text{NO}_3^-$  (SODIUM SALTS ADDED TO DISTILLED WATER).

-- Dotted lines delineate range of observed steady potential in steel

Figure 18. Effect of temperature and bicarbonate concentration on zinc potential (After Hoxeng 6).



SOLUTION COMPOSITION (NOMINAL): 100 PPM  $\text{HCO}_3$ , 10 PPM  $\text{SO}_4$ , pH 7.9 WITH ADDITIONS AS FOLLOWS: CURVE A, NONE; CURVE B, 16 PPM  $\text{SiO}_2$ ; CURVE C, 16 PPM  $\text{SiO}_2$  AND 10 PPM Ca.

-- Dotted lines delineate range of observed steady potential of steel

Figure 19. Effect of temperature on zinc potential in various solutions (After Hoxeng 7).

In tap waters with appropriate iron concentrations, reversal can also be observed. Guest<sup>(9)</sup> demonstrated such reversal in a Toronto tap water with the following analysis:

HCO<sub>3</sub> = 91 ppm  
SO<sub>4</sub> = 23 ppm  
Cl = 20 ppm  
SiO<sub>2</sub> = 0.2 ppm  
pH = 7.8.

In contrast to distilled water solutions where such reversals could be obtained in hours, Guest's water required a minimum of 13 days at 70°C before reversal occurred. At 60°C, 34 days were required and at 80°C and 90°C, 24 and 23 days were required, respectively.

As is accurately noted by Haney<sup>(14)</sup>, the mechanism by which the zinc becomes ennobled is not clear. While the reversal has been attributed to the build-up of corrosion products<sup>(15)</sup> or to passive film formation on the zinc<sup>(13)</sup>, which mechanism is actually operative may depend on the anion responsible for the polarity reversal<sup>(16)</sup>.

To determine if Colorado River water, State Water Project water (SWP), or local well water would provide conditions necessary for potential reversal, the bench-scale system shown in Figure 20 was set up. A 1400 ml beaker containing the test solution was set on a hot plate and stirred continuously. Air was bubbled in through an air stone to maintain dissolved oxygen. An iron electrode (iron pipe) and zinc electrode (zinc ribbon) were suspended in the solution together with a silver/silver chloride reference electrode. A digital volt meter connected to the reference electrode and either the iron or the zinc electrodes provided voltage readings. For long-term tests a mechanical siphon system brought in deionized water as the level in the beaker dropped.

To ensure that the system worked, a preliminary test was carried out using distilled water with 110 mg/L HCO<sub>3</sub>, 10 mg/L SO<sub>4</sub>, and 10 mg/L NO<sub>3</sub> as the electrolyte. The intent was to duplicate Hoxeng's results shown in Figure 18. A relatively good agreement was obtained, as is shown by Figure 21.

A sample of SWP water was then tested. Figure 22 illustrates no measurable potential reversal after 100 hours. While the levels of bicarbonate; sulfate, and chloride make potential reversal possible, the high level of silica in SWP water probably prevented such reversal from occurring.

Colorado River water (CRW) was similarly tested, with similar results (Figure 23). In this case, however, the high sulfate concentration is the most likely cause for the lack of reversal. The next solution tested was CRW with 4 mg/L of copper and 2 mg/L citric acid. As shown by Figure 24, this did not alter the results obtained with Colorado River water alone.

A final test was run using Pasadena tap water during a period when the supply was being taken from local wells. Well water bicarbonate averages around 175 mg/L, while sulfate, chloride and silica are all low (around 35 mg/L, 20 mg/L and 2 mg/L, respectively). Thus this water seemed a likely candidate for potential reversal. Figure 25, however, shows that no reversal occurred after a test period of 90 hours.

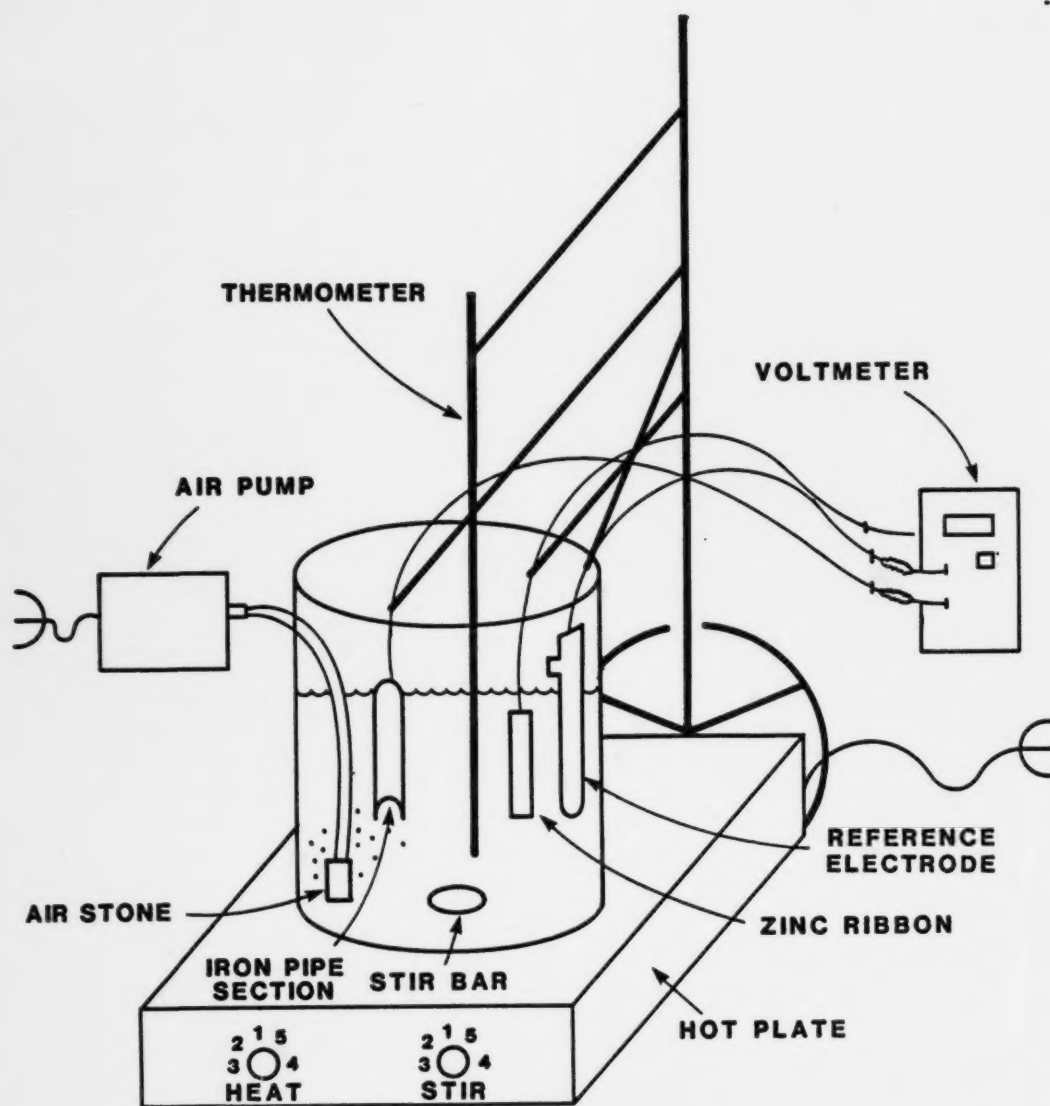


Figure 20. Bench scale apparatus for testing potential reversal.



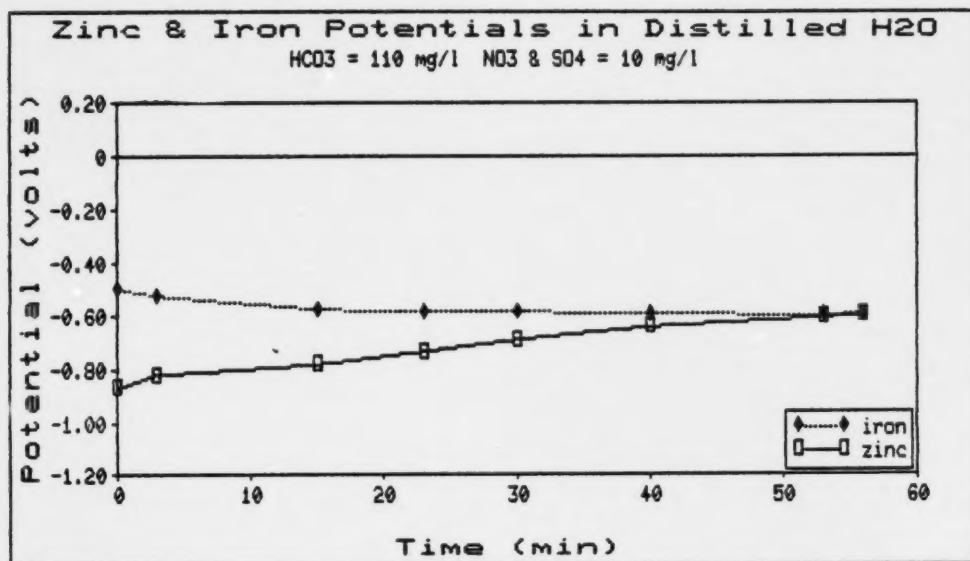


Figure 21. Zinc and iron potentials in distilled water with added salts.

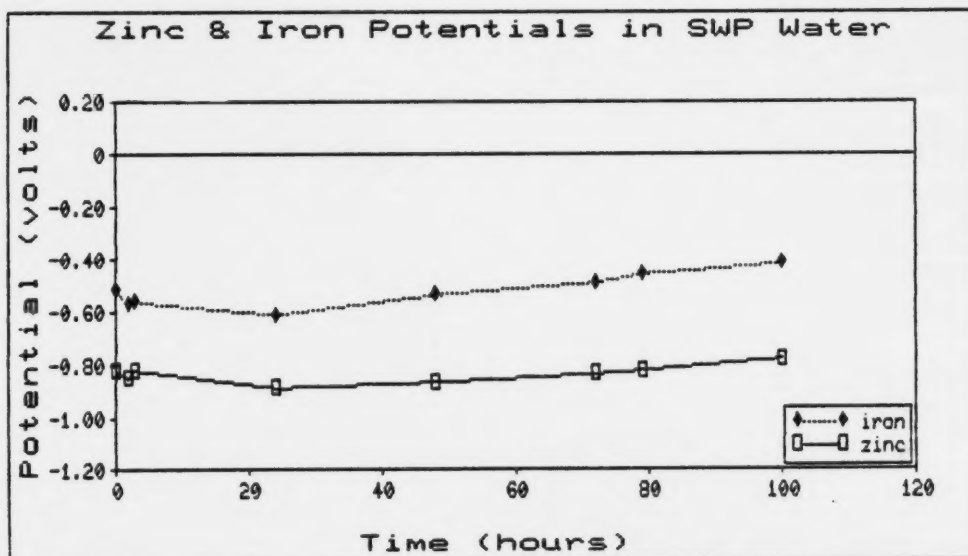


Figure 22. Zinc and iron potentials in SWP water.

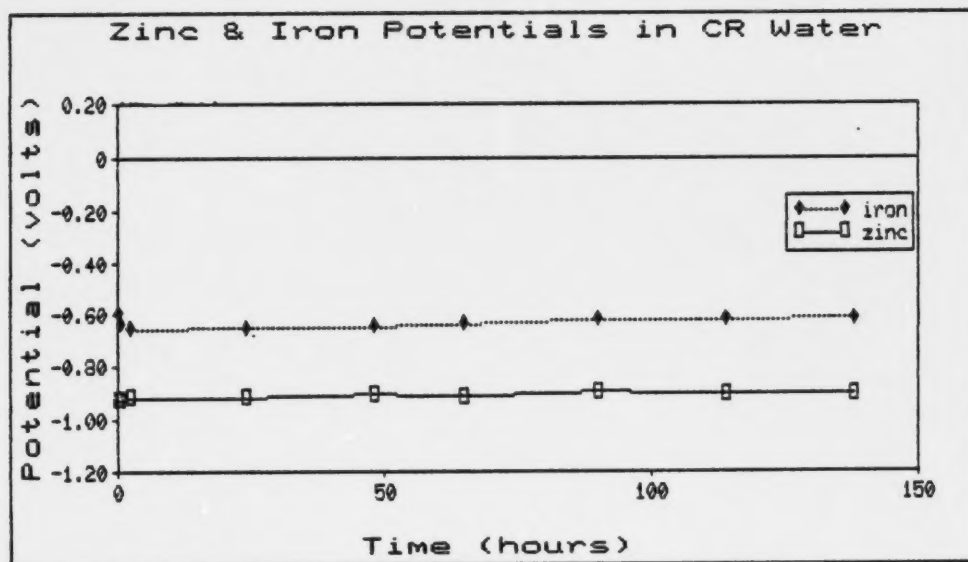


Figure 23. Zinc and iron potentials in CRW.

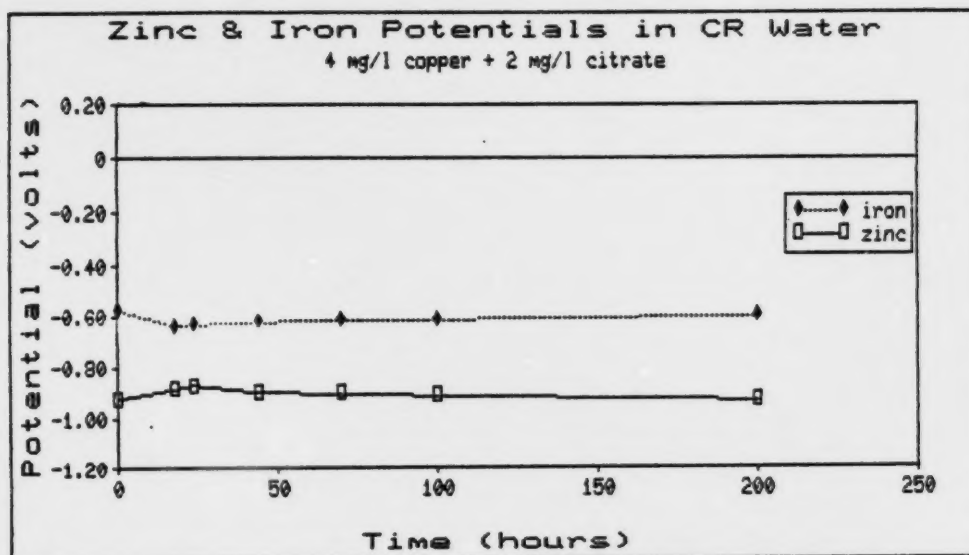


Figure 24. Zinc and iron potentials in CRW with 4 mg/l copper and 2 mg/l citrate.

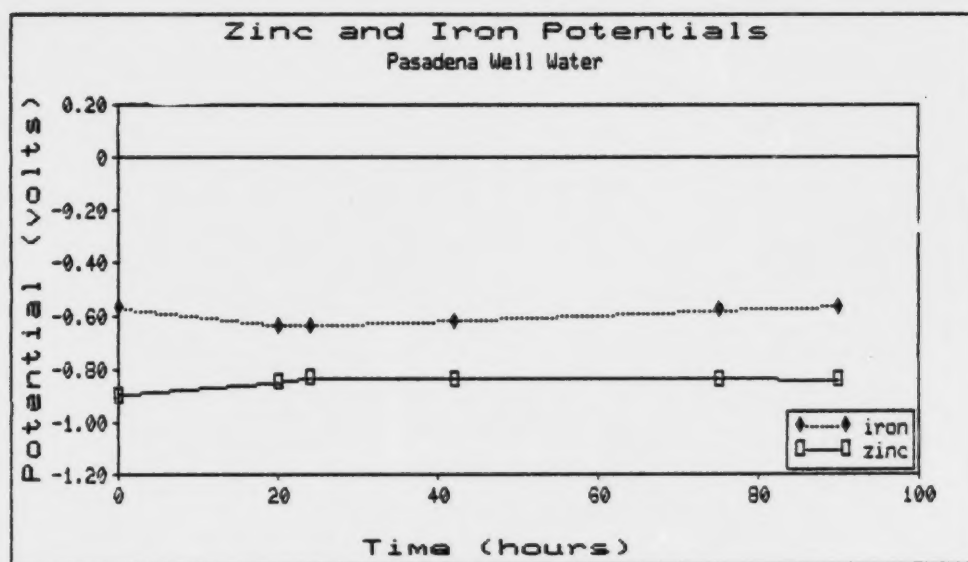


Figure 25. Zinc and iron potentials in Pasadena well water.

## PIPE SURFACE ANOMALIES

Two sets of tests were conducted to examine the effect of the pipe surface anomalies on the corrosion process. The first was qualitative and utilized deionized water containing various copper and citrated-copper solutions. The second was quantitative (based on pit depth measurements) and utilized tap water as a basis for similar solutions. In both tests, the surfaces of 3-inch pieces of galvanized steel pipe (Korean) were mechanically altered (via acid etching and/or drilling) or left intact (controls). Replicate sets of the test pipes were then placed in glass pans containing different test solutions and the pans were in turn set in a constant temperature bath at 50°C. Each pan was aerated throughout the test period.

### Corrosive Influence of Copper and Citrated Copper in Distilled Water

The first bench test operated for six weeks between November 7 and December 15, 1983. Table 9 indicates the solutions tested and whether (+) or not (-) localized corrosion occurred. As shown, the solutions containing salt (at 2,000 mg/L) showed no apparent corrosion. The lack of activity was attributed to the rapid buildup of a soft, white deposit over the pipe surfaces. This buildup effectively protected the surface from reaction. After the system was shut down and the pipes stripped of their deposits, obviously some zinc loss had occurred, but no substantial corrosion occurred under the deposits.

In the solutions without salt, some localized corrosion appeared in and around the drilled pits. Figure 26 illustrates that the two pipes having drilled holes showed localized corrosion activity near the pits in each of the four solutions. (The corrosion occurring along the cut edges results from a poorly bonded epoxy coating, and the reddish particulate matter overall derives from these same edges). The pipes were then stripped with inhibited sulfamic acid. In spite of the high copper or citrated copper doses, underneath the scale and corrosion product, little pitting corrosion actually occurred. Since no measurements of pit depth or pipe weight prior to the test were made, any quantitative assessment of corrosion were precluded.

### Corrosive Influence of Copper, Citrated Copper, and Azurite Particles in Tap Water

The second bench test was operated for eight weeks between January 4, and February 28, 1984. Six test solutions and test pipes were prepared as outlined in Table 10. Both before and after stripping, these pipes showed substantially more evidence of corrosion than did those from the previous bench test. Figures 27 and 28 (pipes from solutions 3 and 6 in Table 10) illustrate results which were typical for each of the six test solutions.

A substantial amount of carbonate material and corrosion product built up over the surfaces of the pipes. The reddish hue on all samples, however, is apparently derived from corrosion of the black iron pipe, not the galvanized samples. The second pipe in the series was shallow drilled through the zinc layer. The third pipe in the series was "spot etched" in the two relatively clear areas. After stripping, a substantial loss of zinc from the galvanized samples was evident. However, no particular corrosion activity around either the drilled pits or the acid etched spots was apparent. No difference among the various solutions (copper, copper and citrate, or tap water) was noted.

TABLE 9  
INFLUENCE OF COPPER AND CITRATED COPPER  
ON CORROSION OF PIPE SURFACE ANOMALIES

| Solution                                         | Pipe Preparation <sup>a</sup> | Observed Corrosion  |                     |
|--------------------------------------------------|-------------------------------|---------------------|---------------------|
|                                                  |                               | Salt<br>(2000 mg/l) | No Salt<br>(0 mg/l) |
| 1 mg/l CuSO <sub>4</sub>                         | Control                       | -                   | -                   |
|                                                  | Etched                        | -                   | -                   |
|                                                  | Etched, drilled               | -                   | +                   |
|                                                  | Control, drilled              | -                   | +                   |
| 1 mg/l CuSO <sub>4</sub><br>0.5 mg/l Citric Acid | Control                       | -                   | -                   |
|                                                  | Etched                        | -                   | -                   |
|                                                  | Etched, drilled               | -                   | +                   |
|                                                  | Control, drilled              | -                   | +                   |
| 0 mg/l CuSO <sub>4</sub><br>Copper Plated        | Control                       | -                   | -                   |
|                                                  | Etched, plated                | -                   | -                   |
|                                                  | Etched, drilled, plated       | -                   | +                   |
|                                                  | Control, drilled, plated      | -                   | +                   |
| 0 mg/l CuSO <sub>4</sub>                         | Control                       | -                   | -                   |
|                                                  | Etched                        | -                   | -                   |
|                                                  | Etched, drilled               | -                   | +                   |
|                                                  | Control, drilled              | -                   | +                   |

- a    Control: Nothing done to pipe sample  
       Etched: Pipe rinsed with dilute nitric acid  
       Etched, drilled: Pipe rinsed with dilute nitric acid, 2 "pits" drilled through zinc layer  
       Control, drilled: 2 "pits" drilled through zinc layer



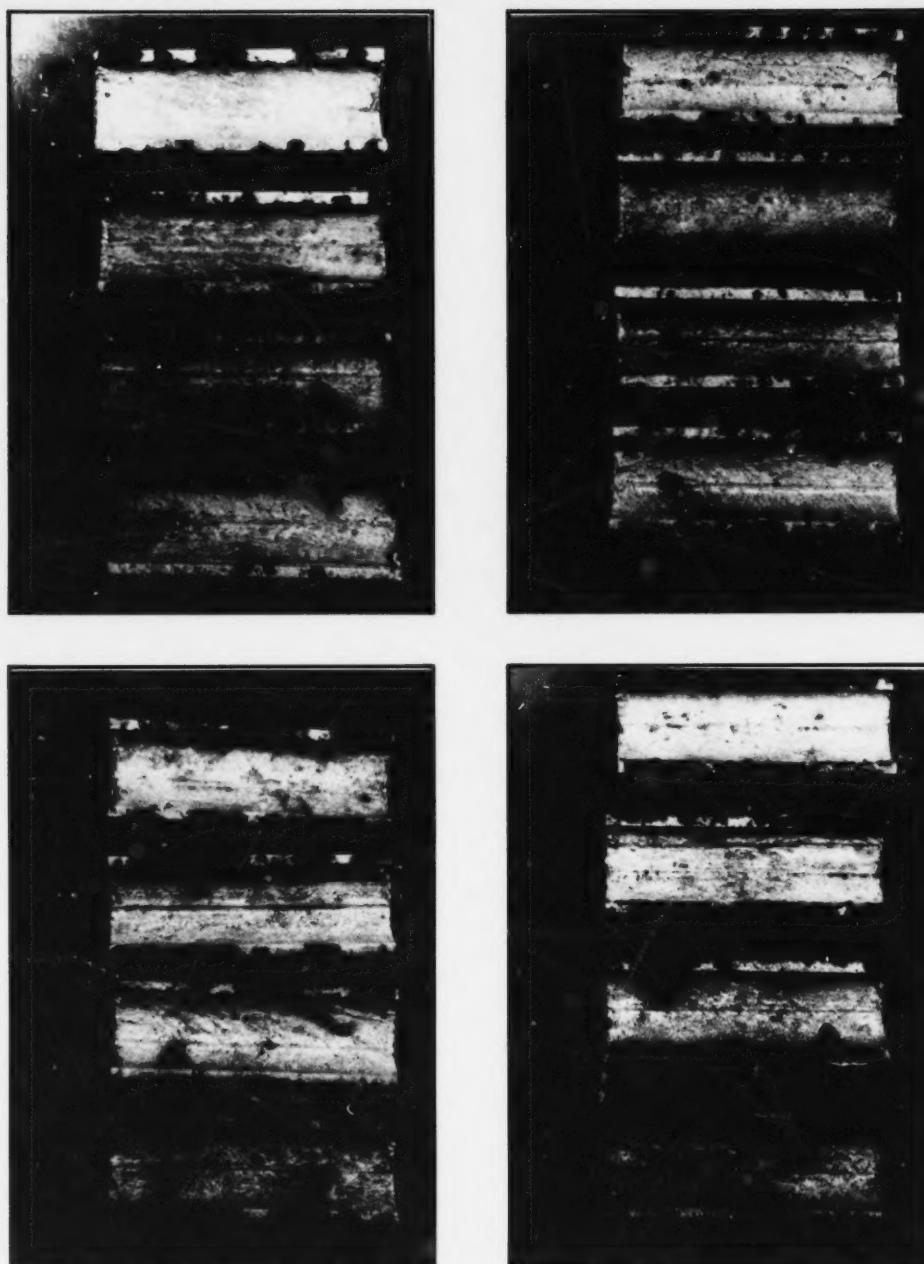


Figure 26. Localized corrosion in vicinity of holes in zinc layer. Test solutions employed are (clockwise from lower left) 0 mg/L  $\text{CuSO}_4$ , 1 mg/L  $\text{CuSO}_4$ , 1 mg/L  $\text{CuSO}_4$  + 0.5 mg/L citrate, and copper plating in drilled holes. For each photo the order of pipes shown (top to bottom) is control, etched, etched and drilled, and control drilled.

TABLE 10

INFLUENCE OF COPPER, CITRATED COPPER AND  
AZURITE PARTICLES ON CORROSION OF  
PIPE SURFACE ANOMALIES

| Solution                                                                 | Pipe Preparation                                                                          |
|--------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|
| 1. 2 mg/l $\text{CuSO}_4$ (as Cu)<br>Tap water                           | Cleaned control<br>Cleaned drilled<br>Cleaned, spot etched<br>Black iron, cleaned control |
| 2. 2 mg/l $\text{CuSO}_4$ (as Cu)<br>1 mg/l citrate<br>tap water         | Same                                                                                      |
| 3. Tap water                                                             | Same                                                                                      |
| 4. 2 mg/l $\text{CuSO}_4$ (as Cu)<br>Azurite particles                   | Same                                                                                      |
| 5. 2 mg/l $\text{CuSO}_4$ (as Cu)<br>1 mg/l citrate<br>Azurite particles | Same                                                                                      |
| 6. Tap water<br>Azurite particles                                        | Same                                                                                      |

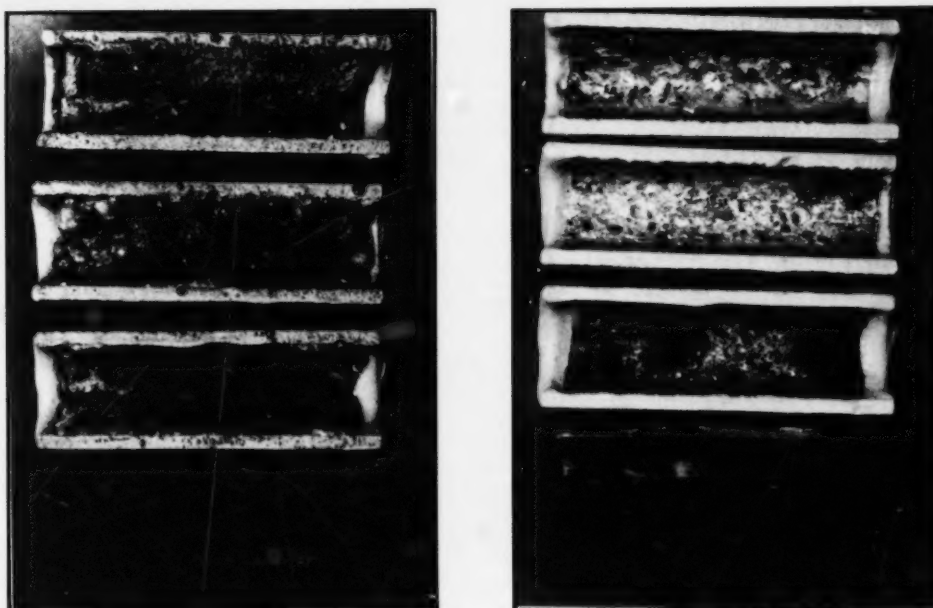


Figure 27. Corrosive influence of local tap water on drilled and etched samples of galvanized steel pipes. The order of samples in both photos (from top to borrom) is control, drilled, spot etched and black iron.

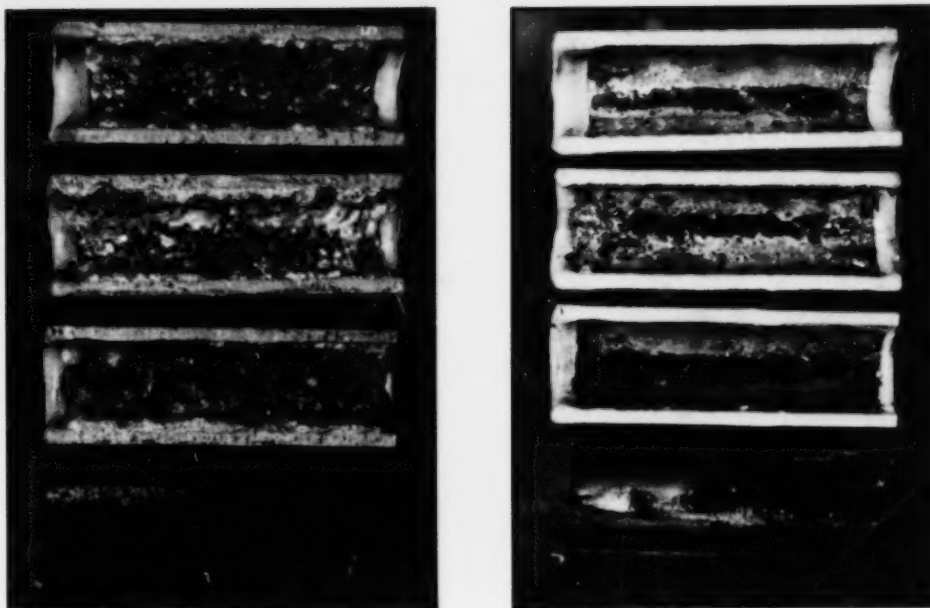


Figure 28. Corrosive influence of local tap water and azurite particles on drilled and etched samples of galvanized steel pipes. The order of samples in both photos (from top to bottom) is control, drilled, spot etched and black iron.

The pipes with azurite particles laid down along their centers (Figure 28) showed this same basic pattern of galvanized corrosion except for a decided increase in zinc loss underlying the azurite. The clearly delineated areas of zinc loss occur along the center line of these test pipes, where the azurite particles rested.

Pit depth measurements made on the drilled pits before and after the test showed no significant differences among pipes which were immersed in tap water or various copper solutions. Table 11 presents these results.



TABLE 11

PIT DEPTH INCREASES AS A RESULT OF COPPER,  
CITRATED COPPER, AND AZURITE PARTICLES  
ADDED TO LOCAL TAP WATER

|    | <u>Solution</u>                                  | <u>Increase in Pit<br/>Depth (mils)<br/>Based on 2 Months<br/>of Immersion</u> | <u>Annualized<br/>Increase in<br/>Pit Depth<br/>(mils)<sup>a</sup></u> | <u>Hypothetical<br/>No. of Years<br/>to pit<br/>Penetration<br/>(No.)<sup>b</sup></u> |
|----|--------------------------------------------------|--------------------------------------------------------------------------------|------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
|    |                                                  |                                                                                |                                                                        |                                                                                       |
| 1. | 2 mg/l Cu                                        | 2.5                                                                            | 15.0                                                                   | 8                                                                                     |
| 2. | 2 mg/l Cu<br>1 mg/l citrate                      | 0.5                                                                            | 3.0                                                                    | 40                                                                                    |
| 3. | Tap water                                        | 1.6                                                                            | 9.6                                                                    | 12.5                                                                                  |
| 4. | 2 mg/l Cu<br>Azurite particles                   | 1.0                                                                            | 6.0                                                                    | 20                                                                                    |
| 5. | 2 mg/l Cu<br>1 mg/l citrate<br>Azurite particles | no change                                                                      | —                                                                      | —                                                                                     |
| 6. | Tap water<br>Azurite particles                   | 0.5                                                                            | 3.0                                                                    | 40                                                                                    |

a Average of two pits on each pipe section.

b Based upon a nominal pipe thickness of 120 mils.

## SECTION 5

### PILOT PLANT INVESTIGATIONS

#### INTRODUCTION

The pilot plant portion of the investigation was designed to test the impact of five major variables: copper dose (0.0, 0.05, 0.10, 0.5, and 5.0 mg/L), pipe manufacturer (Australian, Korean, and U.S.), initial mode of exposure (static, flowing), water quality (CRW, SPW), complexing agent (citrated, un-citrated) on the corrosion rate of galvanized steel pipe. Because of the magnitude of the undertaking and the length of time for achieving equilibrium corrosion rates, some testing was performed sequentially, and the effect of citric acid was studied at only one copper dose (5.0 mg/L). More details are provided in the following subsections on system design, operation, water quality, pipe analyses, and results.

The pilot plant was designed and constructed in 1981, and operated between February 1982 and February 1984. It was located in an underground vault at the MWD's Weymouth Plant in La Verne, California. The vault housed a venturi structure on the Weymouth plant's influent line for State Project Water. The pilot plant tied into this structure directly for its SWP test supply. For CRW, a temporary pipeline was constructed from a nearby vault housing the Weymouth plant's influent line for CRW.

The intent of the pilot plant design was to simulate household operations, with water supplied from a local reservoir entering the house, being heated and distributed. An on/off flow pattern occurred during the day and no flow occurred at night. As shown in Figure 29, influent water entered six replicate test lines, each consisting of a chemical feed station, a detention tank, a water heater, and a set of six lengths of test pipes. The chemical feed (of copper sulfate) and the detention tank were intended to simulate a local reservoir with copper addition for algae control. The water heater and test pipe then simulated piping within individual houses. To avoid contamination in the test system, all of the piping and valving leading up to the test pipes were composed of PVC or CPVC. Similarly, the detention tanks and heaters were glass lined. The test pipes themselves were ASTM A120 galvanized steel pipe.

The design allowed consideration of five variables during two phases of work: (1) copper dose, (2) pipe type, (3) mode of exposure of the test pipe to the water (static versus flowing), (4) water quality, and (5) the use of citrated versus uncitrated copper. Figure 30 provides a time line to describe the order of variable testing. Phase 1 occurred for the duration of the pilot plant operations, i.e., February 1982 to February 1984. During this phase, raw Colorado River water (CRW) and six doses of copper (0.0, 0.05, 0.10, 0.5, 1.0, and 5.0 mg/L) were tested. For each dose, six lengths of test pipe were exposed, two Korean, two Australian, and two U.S. Of each pair, one pipe length was initially filled with test water and its designated copper dose and allowed to sit with no in-flow or out-flow for three months. This was intended to simulate a

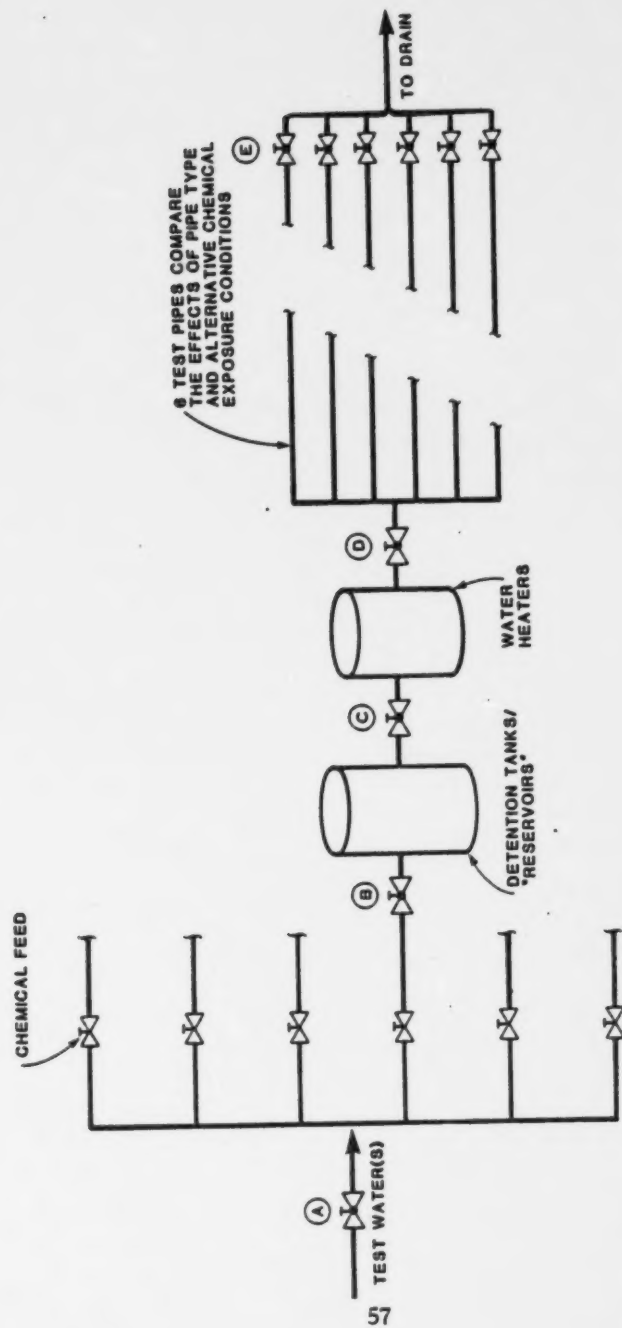


Figure 29. Schematic of pilot facilities, including locations of water quality sampling valves A - E

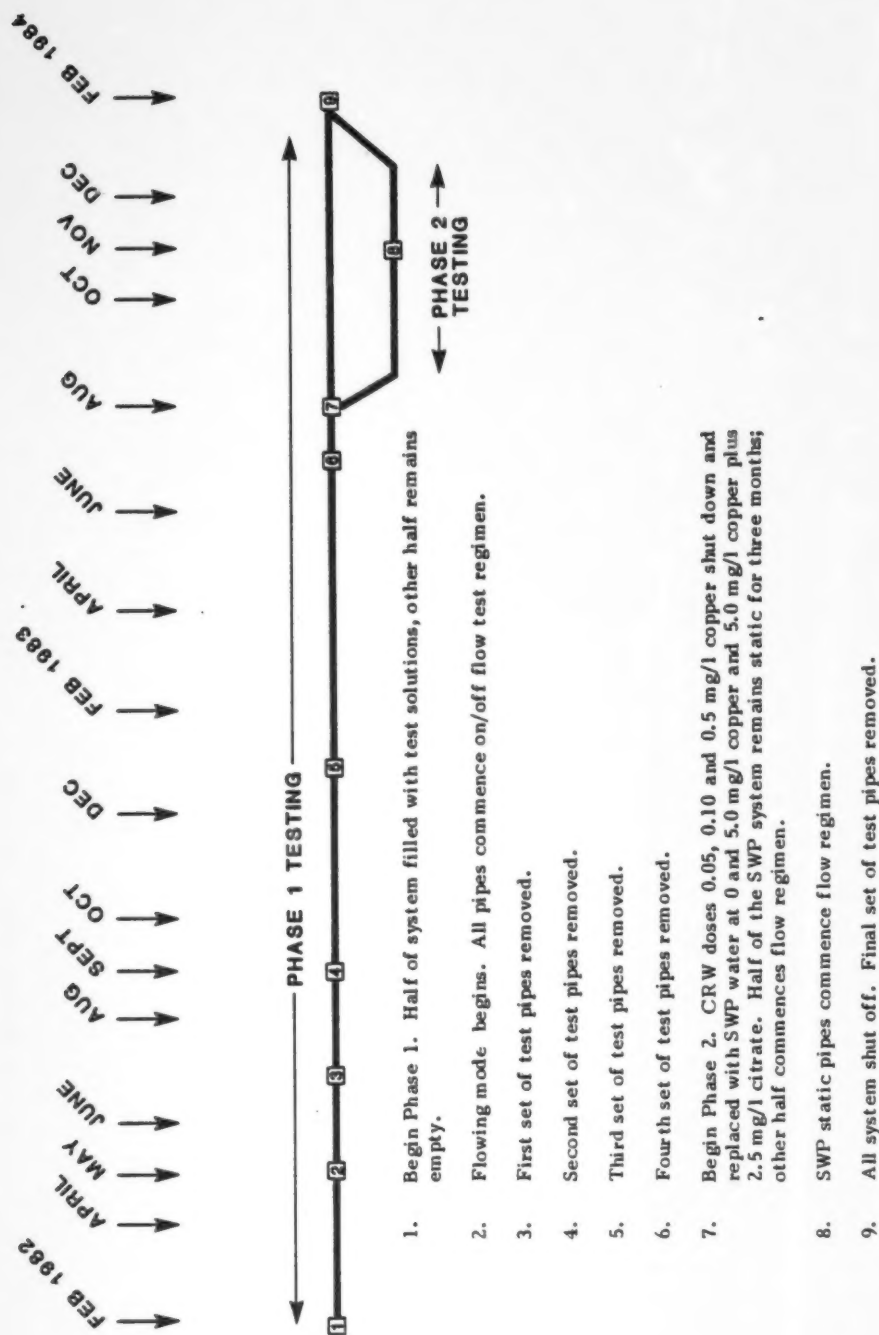


Figure 30. Pilot plant testing time line.

condition wherein a set of new houses would be built, but not sold immediately. The water utilized during plumber's leak testing would thus simply sit in the pipes until occupancy. If copper was in the water during this leak testing, the pipe would have a period of static exposure to the copper solution.

The alternate "mode of exposure" was experienced by the other half of each pair of the test pipes. From the beginning, these were incorporated into the flow cycling of the system; thus the pipes were exposed to new doses of copper laden water with each flow cycle.

Phase 2 operation overlapped Phase 1, beginning in August 1983 and ending in February 1984. Phase 2 evaluated the fourth and fifth variables, water quality and citrated versus uncitrated copper. To do this, half of the Phase 1 system was shut down, the test pipes replaced, and the influent water changed to raw State Water Project (SWP) water. Copper doses tested on this supply were: 0, 5.0 mg/L, and 5.0 mg/L plus 2.5 mg/L citrate. Again, there were six pipes associated with each dose and half of each set of six received initially static exposure to the test solutions over a three month period.

Each 28 foot length of test pipe was actually composed of seven, 4 foot sections connected with polyurethane tubing and clamps. This allowed sections to be removed periodically for examination without disturbing the entire system.

#### OPERATION

Once constructed, the pilot plant was in a large part self-operating. Test water cycled intermittently through the system for 15 hours each day and bypassed it for nine hours each night. The 15 hours of daytime cycling were broken down into 3 hour increments. For the first 10 minutes of each increment, one from each set of six test pipes would receive flow. The entire system would then be bypassed for the next 2 hours 50 minutes. Flow would then pass onto the next set of six for 10 minutes and so on. Thus, each pipe received a 10 minute flow period once every three hours, or for 50 minutes total in 15 hours. Automatic ball valves at the end of each pipe connected to a relay box controlled this cycling.

Chemicals were fed from stock solution tanks via Milton Roy simplex or duplex pumps only when the ball valves were open, and only for a fraction of the time the system operated. The intent was to simulate copper sulfate (or copper sulfate plus citrate) feed to a local reservoir for algae control. This would typically occur only during the summer months and for a few days each month. Thus, the pilot plant received chemical feed for four days a month for five months during year one (May 12 through September 24, 1983) and for five months during year two (August 1984 through December 1984). Flow through each test pipe was set at 12.6 liters per minute (3.3 gallons per minute). Manual valves at the end of each test pipe were opened only enough to allow this amount of flow through. To ensure this rate remained constant, periodic checks with a Kent water meter were made.

The copper sulfate plus citrate solutions were made up in deionized water. A sufficient quantity of stock solution was made up for each required dose to last several days. A check of chemical feed flow was made when the feed pumps operated during each four day operation. Because of the small quantities involved, a modified 500 ml



graduate cylinder was used to monitor this chemical feed. A tap inserted into the bottom of the graduate cylinder could be hooked up to the suction end of the pump and chemical usage monitored.

The detention tanks at the head of the system were sized to provide an hour of detention time after the chemical feed. This time interval was determined from jar tests in which copper sulfate added to tap water was found to reach equilibrium between solid and dissolved phases within an hour.

From the detention tanks, the test water entered 50 gallon water heaters. These brought the water temperature up to 50°C just prior to entry into the test pipe. Commercial electric water heaters were utilized because their temperature controls were more accurate and their recovery time faster than standard household models. Thus, the 20 minute interval between flow into successive pipes was sufficient to allow the temperature of the water within the heaters to re-attain 50°C.

#### WATER QUALITY

Water quality entering, within and exiting the pilot plant was regularly monitored by the MWD. Figure 30 illustrates the sites at which sample taps were located. Station A was the point for influent water quality, Stations B-1 through B-6 for chemical feed, C1 to C6 were immediately after the detention tanks, D1 to D6 after the water heaters, and E1 to E36 exiting the system, after the test pipes.

During the first five months of operation, samples were taken weekly at all sites. Table 12 shows the monthly sample program for each site. As the characteristics of the system became known, fewer samples were required. Eventually routine sampling occurred bi-monthly and consisted of influent sampling of temperature, pH, conductivity (TDS), alkalinity, and calcium. From these measurements, the Langelier Index was calculated. When copper was being added, additional samples for total copper were taken at Stations B1 to B6, D1 to D6, and at six E stations (one for each copper dose).

Table 13 compares SWP and CRW quality as monitored by MWD for fiscal year 1983. Figures 31 through 35 present the results of monitoring these two supplies for pH, alkalinity, TDS, calcium, and Langelier Index ahead of the pilot plant facilities.

As shown, CRW water quality remained very constant throughout the Phase 2 period September 6, 1983 to February 15, 1984, and this was true of Phase 1 as well. The SWP supply was also fairly constant, but became mixed with CRW in November and December when blending upstream of the pilot plant occurred. Increases in pH, alkalinity, TDS, calcium and the Langelier Index are all observed during this time.

#### PIPE ANALYSES

Since each 28-foot length of test pipe was actually comprised of seven, four-foot lengths, sections could be periodically removed for analysis without disturbing the majority of the system. Sections for analysis were removed from the end nearest the water heater (where conditions would be most severe). The remaining six pieces were then moved forward toward the heater and new sections added at the discharge end. This ensured that existing pipes in the system were not exposed to new material from the pipes being added.

TABLE 12  
INITIAL SAMPLING SCHEDULE  
(February - July 1982)

| Station/Week | 1                                                               |                                | 2                                          | 3                                  | 4                                  |
|--------------|-----------------------------------------------------------------|--------------------------------|--------------------------------------------|------------------------------------|------------------------------------|
| A            | pH<br>Alkalinity<br>Copper <sup>a</sup><br>Calcium<br>Magnesium | Silica<br>Zinc<br>Conductivity | pH<br>Alkalinity<br>Copper<br>Conductivity | pH<br>Alkalinity<br>Copper<br>E.C. | pH<br>Alkalinity<br>Copper<br>E.C. |
| B1 - B6      | Copper                                                          |                                |                                            |                                    |                                    |
| C1 - C6      | Copper                                                          |                                |                                            |                                    |                                    |
| D1 - D6      | pH<br>Alkalinity<br>Copper<br>Calcium                           | Magnesium<br>Silica            | pH<br>Alkalinity                           | pH<br>Alkalinity                   | pH<br>Alkalinity                   |
| E1 - E36     | pH<br>Alkalinity<br>Copper                                      | Zinc                           | pH<br>Alkalinity                           | pH<br>Alkalinity                   | pH<br>Alkalinity                   |

a Dissolved and total copper for all analyses.

TABLE 13  
ANALYSES OF MWD WATER SUPPLIES  
1982-83 FISCAL YEAR AVERAGES

| Constituent                           | Symbols and<br>Units |         | Source Waters |      |
|---------------------------------------|----------------------|---------|---------------|------|
|                                       |                      |         | CRW           | SWP  |
| Silica                                | SiO <sub>2</sub>     | mg/l    | 9.2           | 13.0 |
| Calcium                               | Ca                   | mg/l    | 83            | 16   |
| Magnesium                             | Mg                   | mg/l    | 30.5          | 6.5  |
| Sodium                                | Na                   | mg/l    | 106           | 22   |
| Potassium                             | K                    | mg/l    | 4.6           | 1.5  |
| Carbonate                             | CO <sub>3</sub>      | mg/l    | 0             | 0    |
| Bicarbonate                           | HCO <sub>3</sub>     | mg/l    | 150           | 68   |
| Sulfate                               | SO <sub>4</sub>      | mg/l    | 300           | 25   |
| Chloride                              | Cl                   | mg/l    | 93            | 23   |
| Nitrate                               | NO <sub>3</sub>      | mg/l    | 0.6           | 2.25 |
| Fluoride                              | F                    | mg/l    | 0.36          | 0.13 |
| Boron                                 | B                    | mg/l    | 0.14          | 0.15 |
| Total Dissolved Solids                | TDS                  | mg/l    | 702           | 143  |
| Total Hardness as CaCO <sub>3</sub>   | Tot H                | mg/l    | 331           | 67   |
| Total Alkalinity as CaCO <sub>3</sub> | Tot alk              | mg/l    | 123           | 56   |
| Free Carbon Dioxide                   | CO <sub>2</sub>      | mg/l    | 1.5           | 1.5  |
| H <sup>+</sup> Concentration          | pH                   | units   | 8.24          | 7.91 |
| Specific Conductance                  | EC                   | µmho/cm | 1106          | 252  |
| Turbidity                             | TU                   | TU      | 1.1           | 3.6  |
| Temperature                           | T                    | °C      | 16.9          | 13.9 |

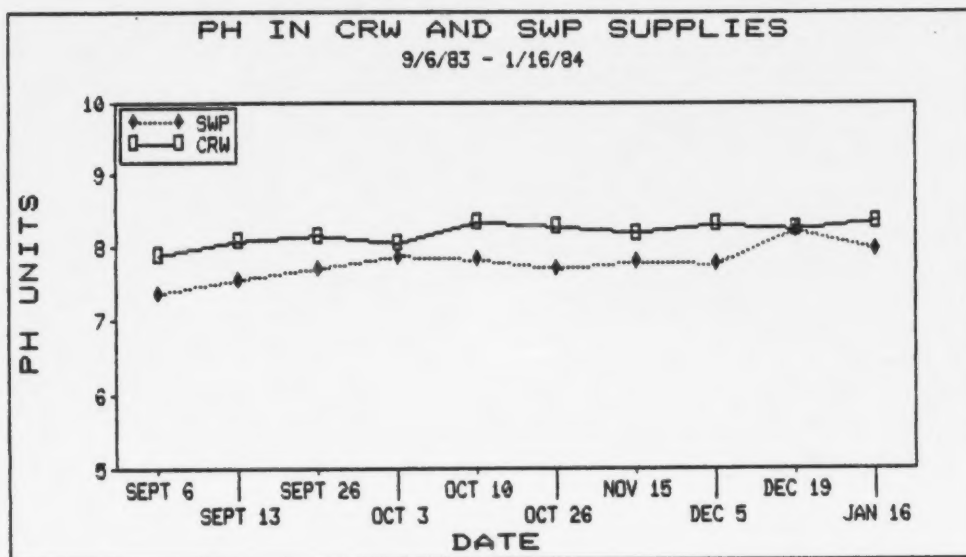


Figure 31. pH in CRW and SWP supplies.

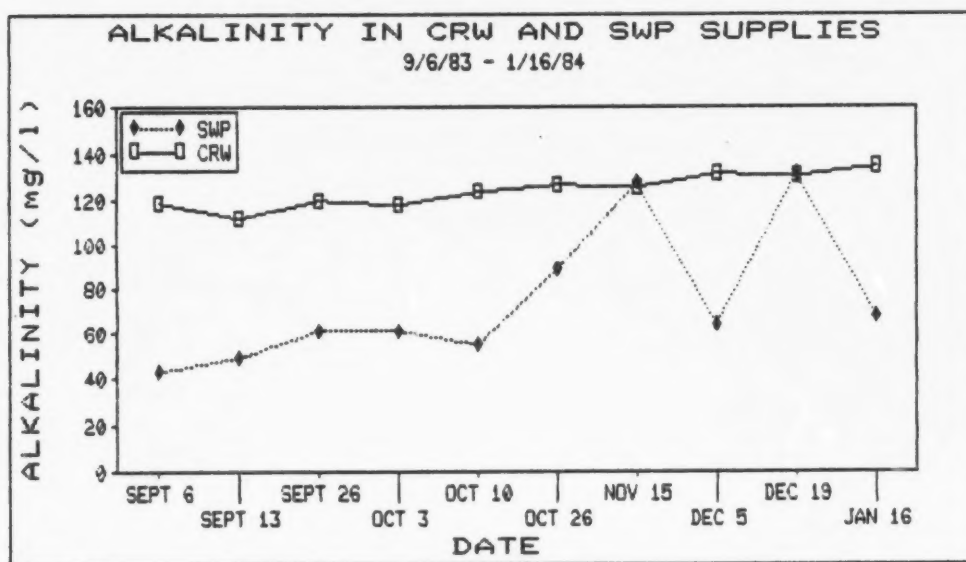


Figure 32. Alkalinity in CRW and SWP supplies.

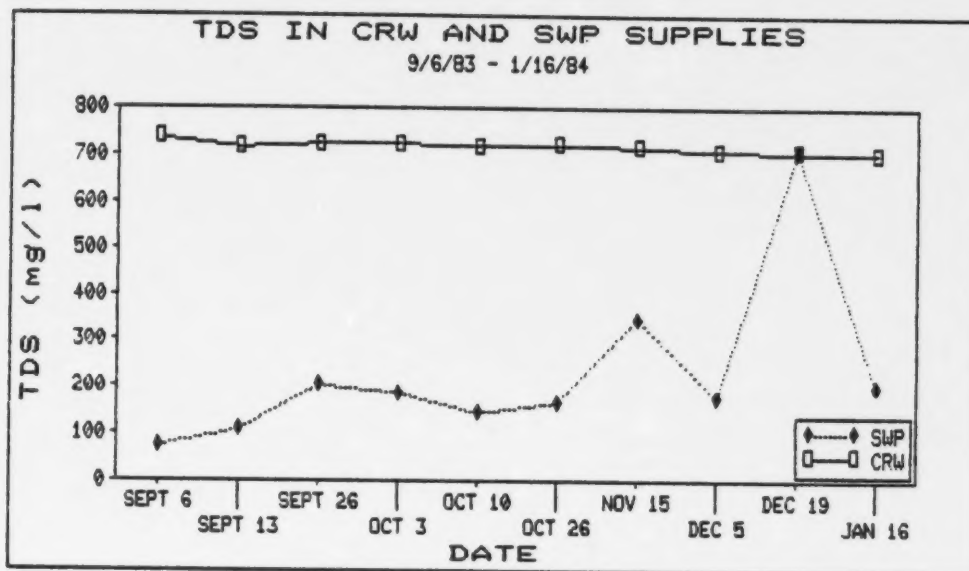


Figure 33. TDS in CRW and SWP supplies.

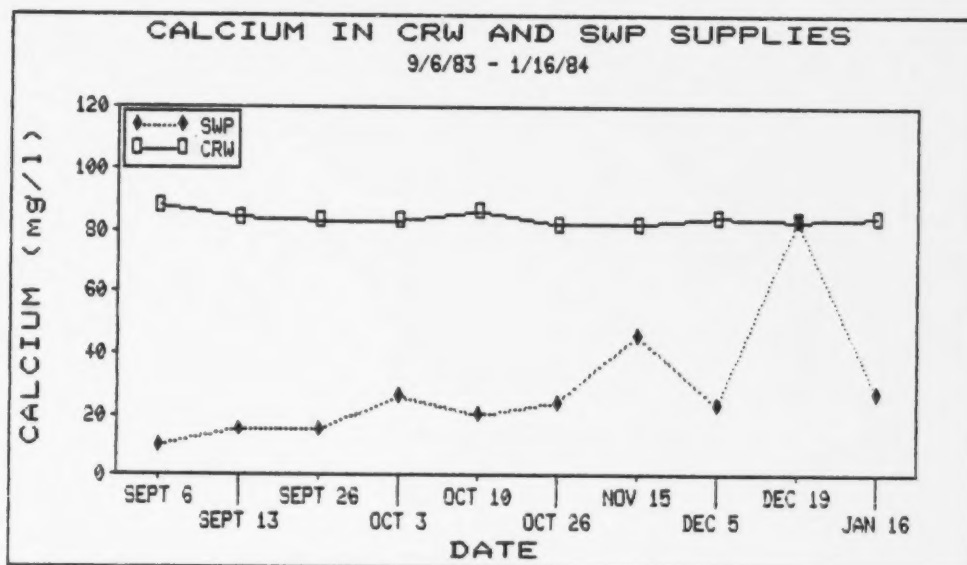


Figure 34. Calcium in CRW and SWP supplies.



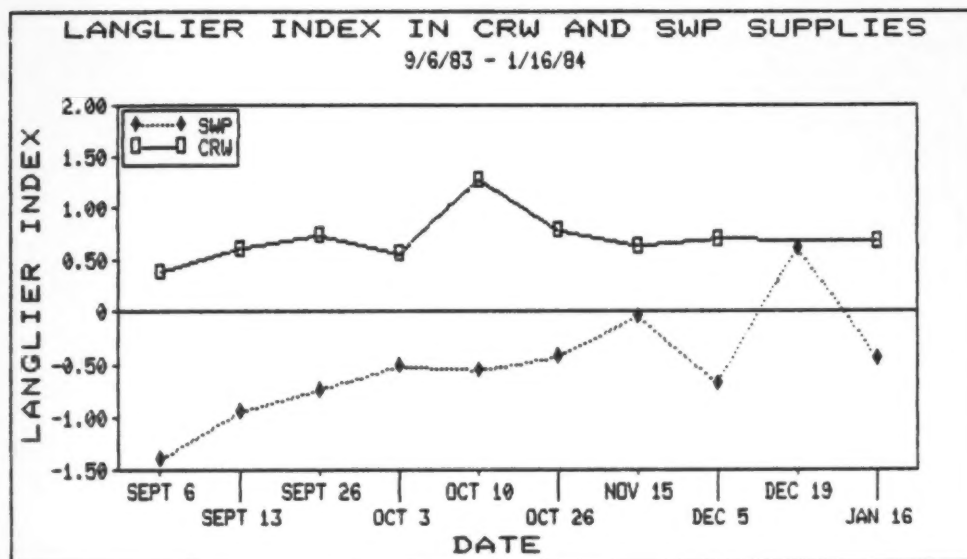


Figure 35. Langelier Index in CRW and SWP supplies.

This process occurred five times. The first set was removed in July 1982 after two months of exposure. The second set was removed in September 1982 after four months of exposure, the third set in January 1983 after eight months of exposure, the fourth set in July 1983 after 14 months, and the fifth set in February 1984 after 20 months of exposure.

Each four-foot section was re-cut into four, one-foot lengths and each length split in half lengthwise to expose the top and bottom. Analysis of the pipes was carried out in several parts. First, one set of one-foot sections (top and bottom) was weighed, stripped with a known amount of inhibited sulfamic acid, and re-weighed. The weight loss represented the total amount of scale on each pipe. The sulfamic acid was then analyzed for calcium, zinc, iron, and copper to ascertain their representative contributions to the scale. Results of analyses done on sections of pipe were subtracted from the scale analyses. Sections of stripped pipe were then analyzed via X-ray fluorescence to determine the relative amounts of zinc and iron on the surface. (A greater iron to zinc ratio indicated greater corrosion activity). Since the pits were never more than superficial, no depth measurements were made. Finally, photographs of sections of pipe with scale and after stripping were made.

This procedure was carried out for the second, third, and fifth pipe sets removed. Apparent changes in the test pipes between the third and fourth sets did not warrant complete analysis of the latter. However, samples of this fourth set were sent to Dr. Jerome Thomas for evaluation. Drs. Thomas and Robert Ray (metallurgists) carried out analysis on these corroded sections along with the new pipes described in Section 3.

## RESULTS

### Photographic Records

Figure 36 provides a key to the layout of pipes for Figures 37-45. Figures 37, 38, and 39 show the scaled and stripped pipes taken from the pilot plant after four months of exposure to doses of 0, 1.0, and 5.0 mg/L copper, respectively. The Korean pipe looks the most scaled and show the most underlying surface deterioration for each dose, while the Australian and U.S. pipes all appear to be in relatively good shape. No apparent differences exist among the different doses or between the static versus flowing exposure pairs.

Figures 40, 41, and 42 show results for pipes taken from the system after 20 months of exposure to 0, 1.0, and 5.0 mg/L copper. Greater scale buildup and more surface deterioration of the stripped pieces has occurred in the 16 additional months of exposure, but none of the pitting penetrates significantly into the pipe. Again, the Korean looks somewhat worse than either the U.S. or Australian, but differences among the three doses or between the static and flowing pairs do not appear to exist.

Figures 43, 44, and 45 show results for pipes for Phase 2, i.e., pipes exposed to SWP for seven months at doses of 0, 5.0 mg/L, and 5.0 mg/L copper plus 2.5 mg/L citrate. They appear similar to the 20 month CRW pipes in degree of surface deterioration, which may be caused by the somewhat more corrosive quality of SWP water. No discernable difference exists between the doses of copper and copper plus citrate, or between the static and flowing pairs.



Figure 36. Pipe appearance, before and after cleaning, after 4 months exposure to CRW with no added copper. Clockwise from upper left: Australian pipe, Korean pipe and U.S. pipe.

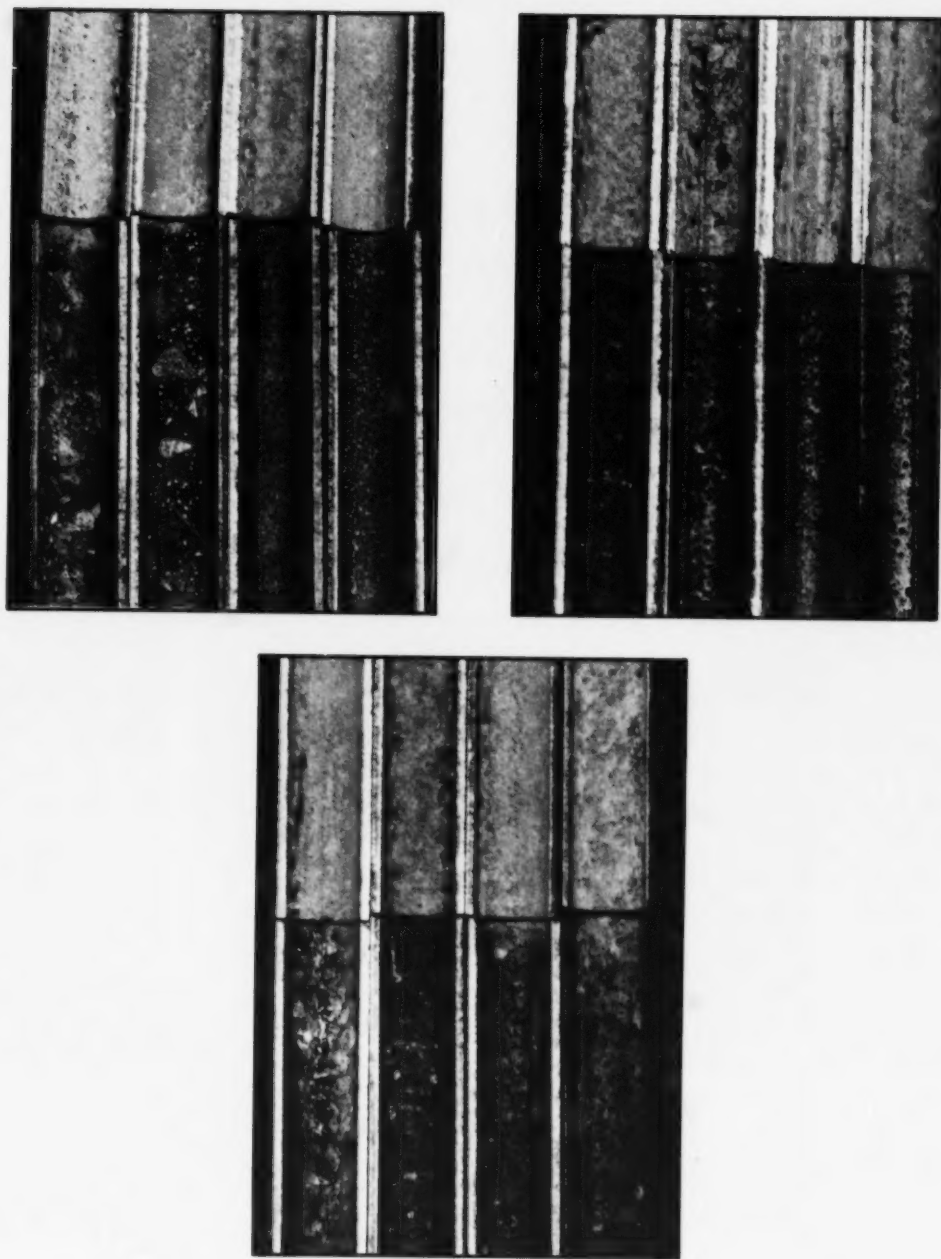


Figure 37. Pipe appearance, before and after cleaning, after 4 months exposure to CRW with 1.0 mg/L added copper. Clockwise from upper left: Australian pipe, Korean pipe and U.S. pipe.

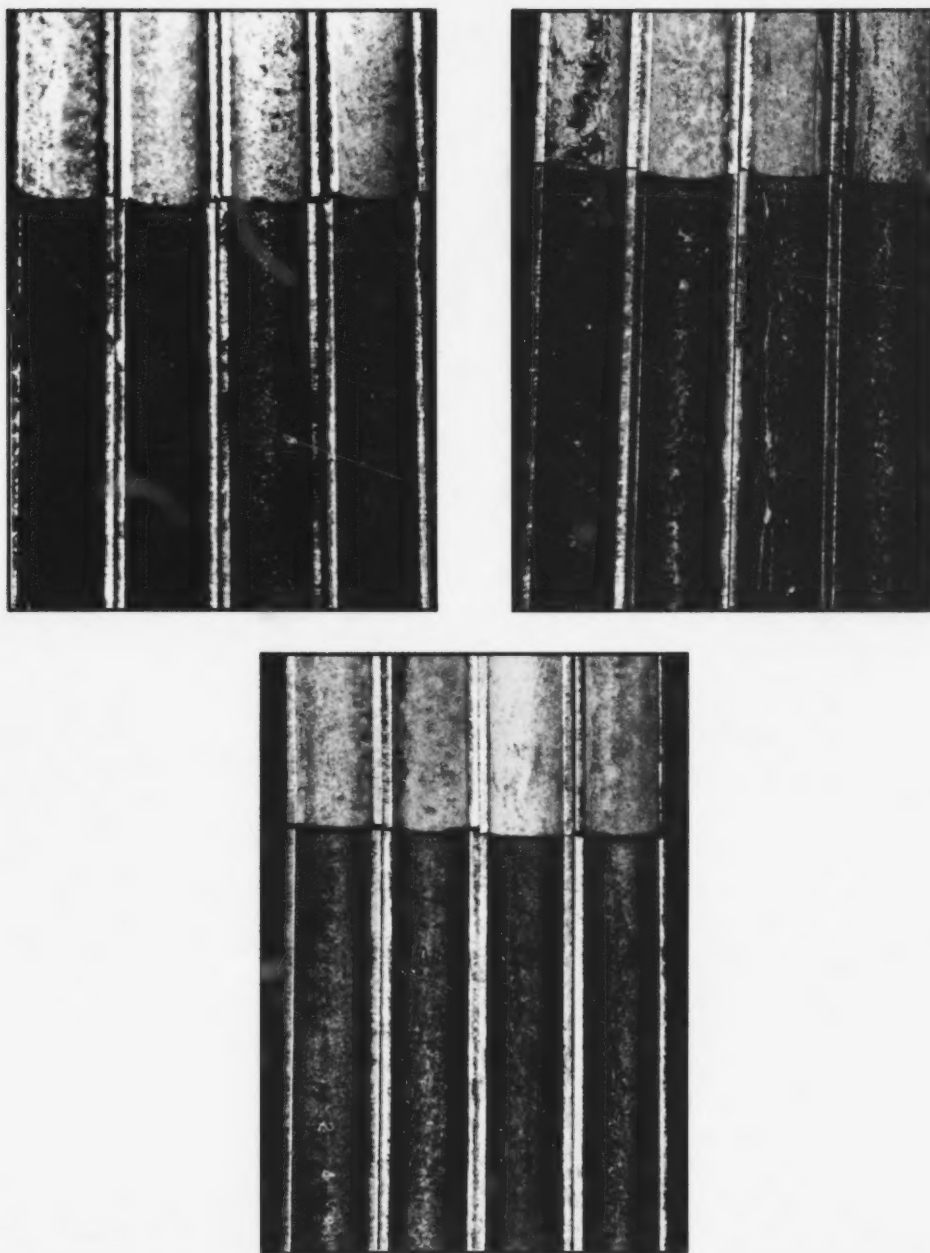


Figure 38. Pipe appearance, before and after cleaning, after 4 months exposure to CRW with 5.0 mg/L added copper. Clockwise from upper left: Australian pipe, Korean pipe, and U.S. pipe.



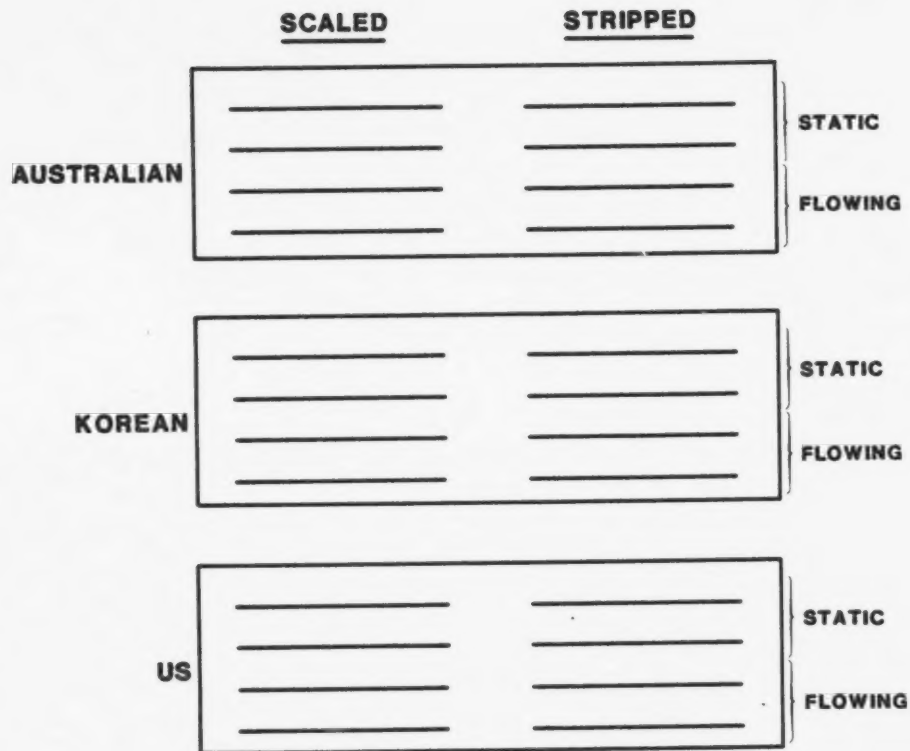


Figure 39. Pipe identification diagram.

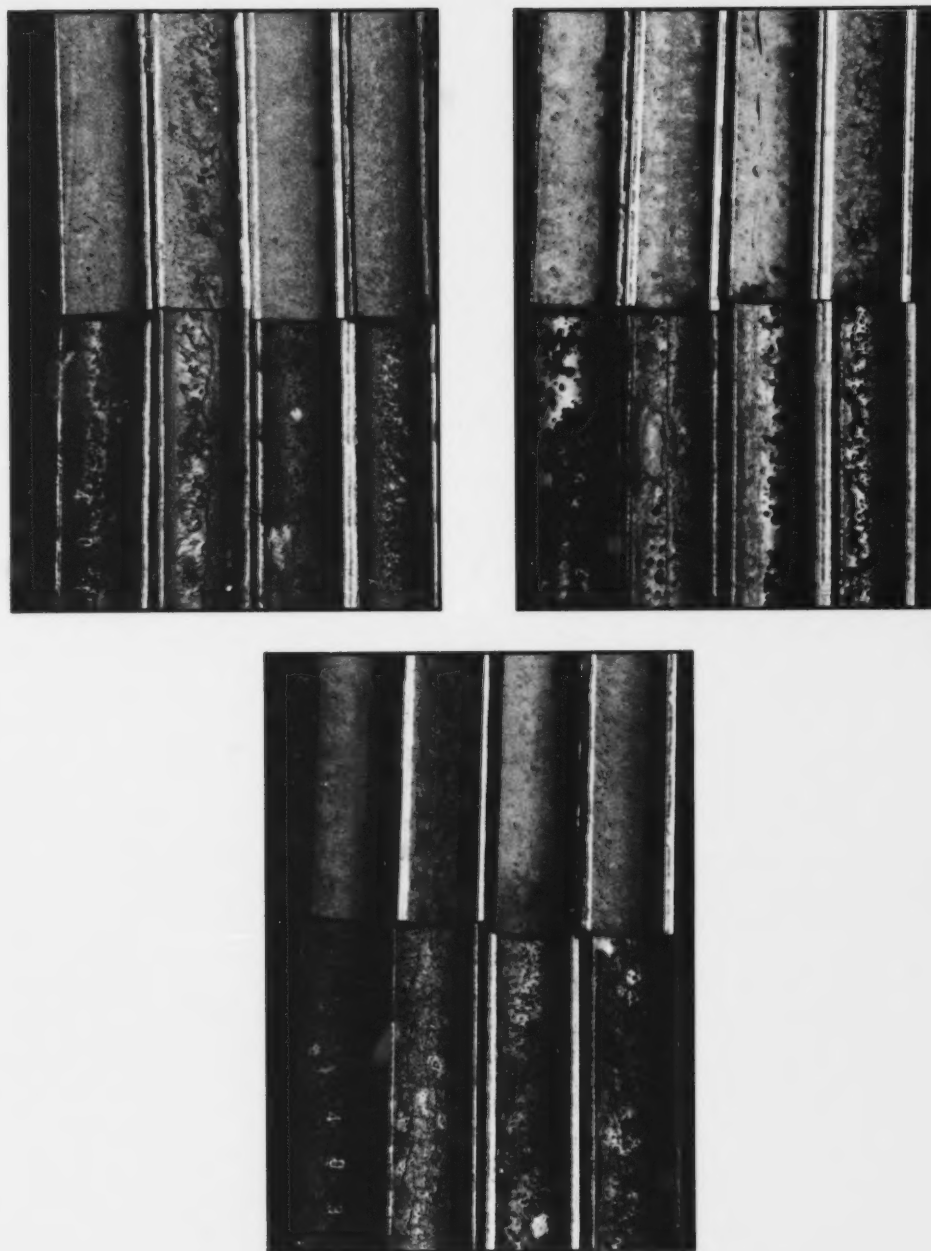


Figure 40. Pipe appearance, before and after cleaning, after 20 months exposure to CRW with no added copper. Clockwise from upper left: Australian pipe, Korean pipe and U.S. pipe.

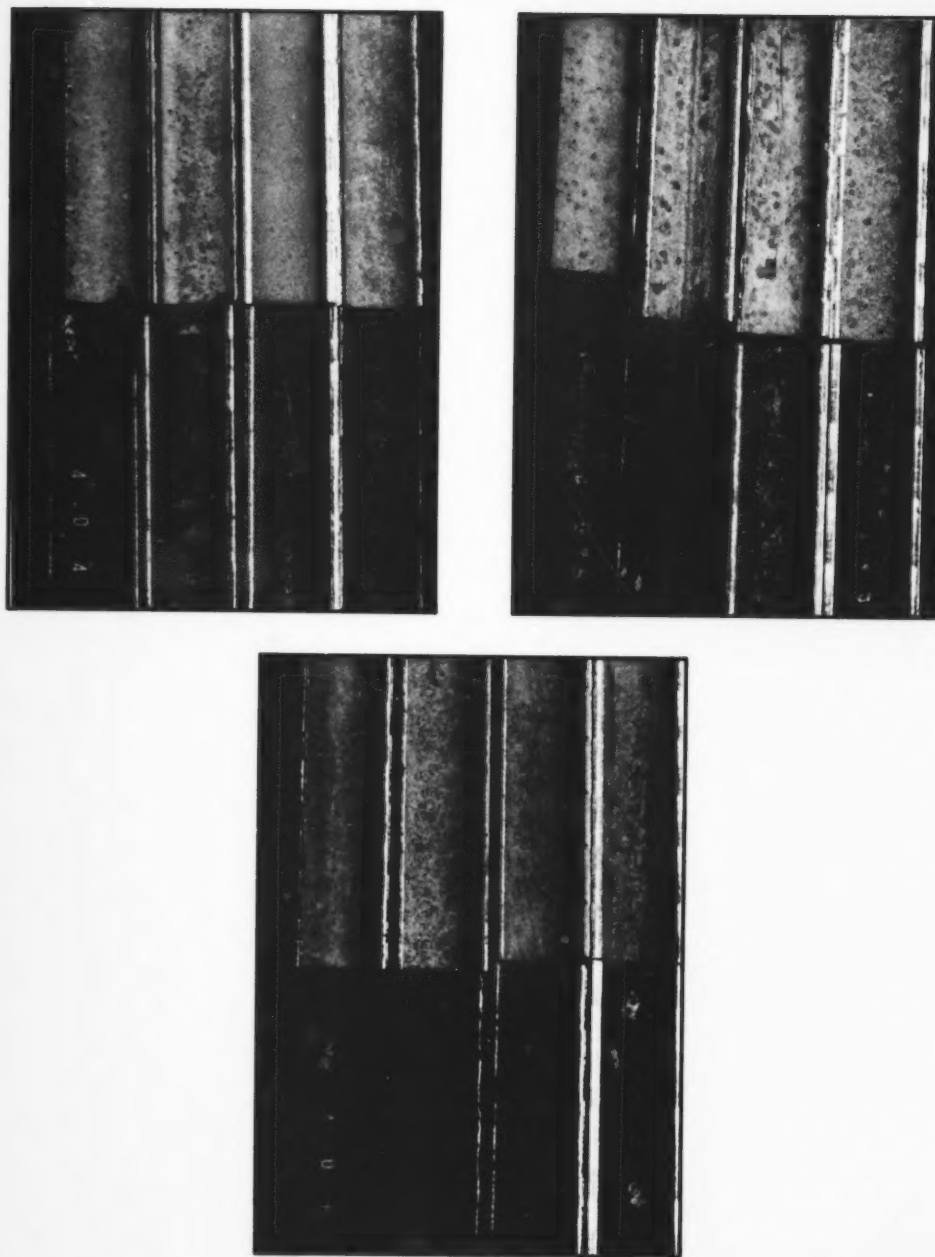


Figure 41. Pipe appearance, before and after cleaning, after 20 months exposure to CRW with 1.0 mg/L added copper. Clockwise from upper left: Australian pipe, Korean pipe and U.S. pipe.

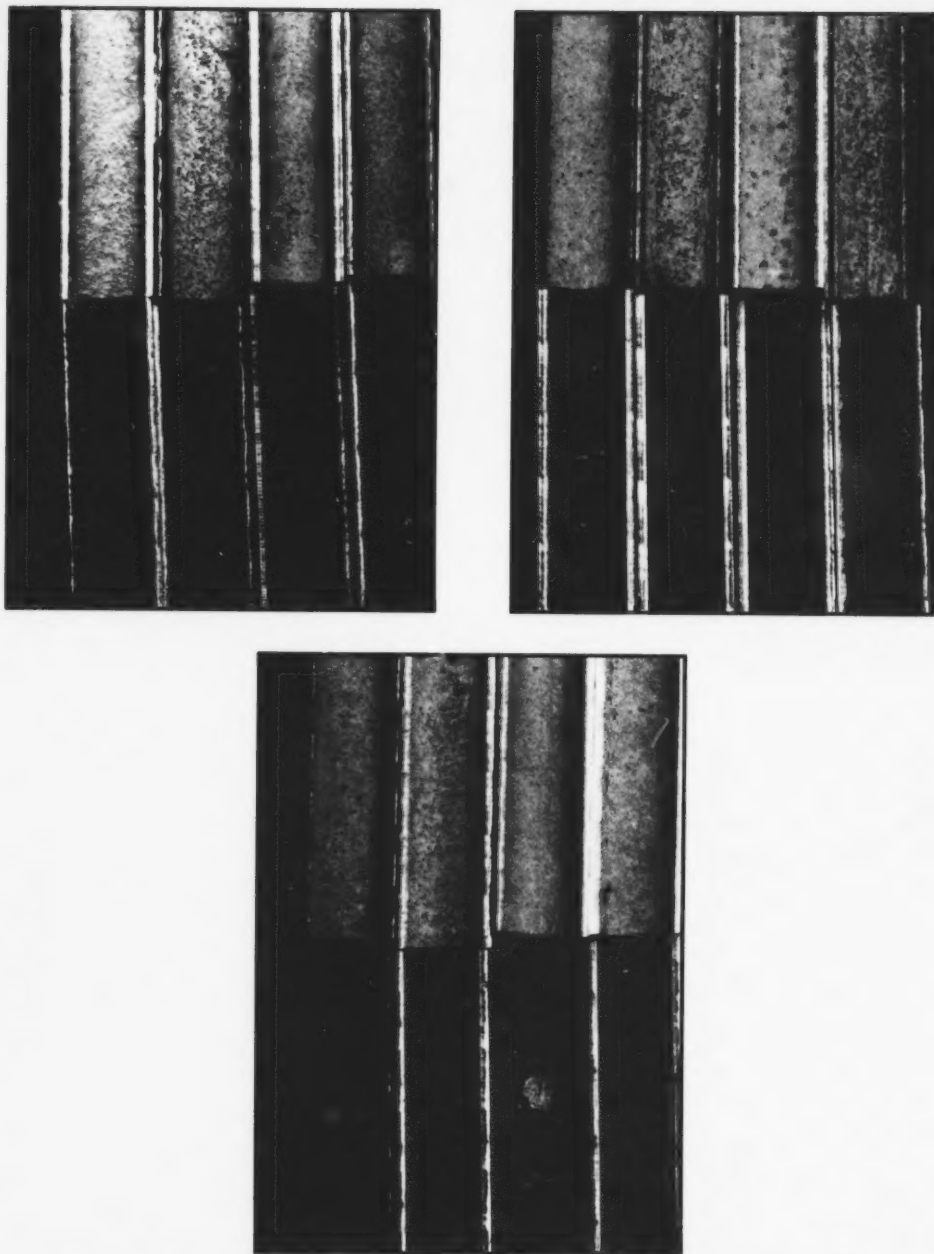


Figure 42. Pipe appearance, before and after cleaning, after 20 months exposure to CRW with 5.0 mg/L added copper. Clockwise from upper left: Australian pipe, Korean pipe and U.S. pipe.

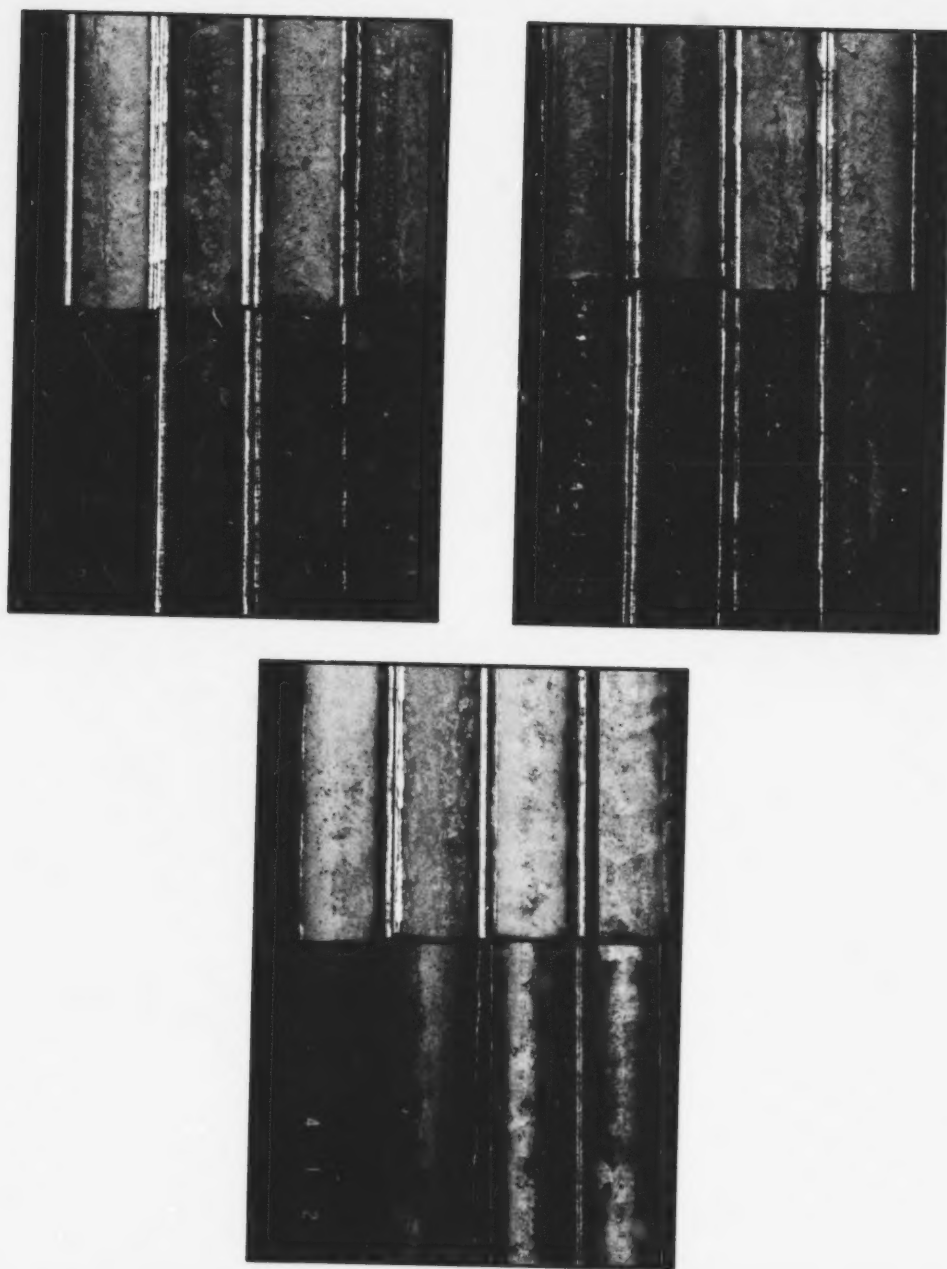


Figure 43. Pipe appearance, before and after cleaning, after 7 months exposure to SWP with no added copper. Clockwise from upper left: Australian pipe, Korean pipe and U.S. pipe.



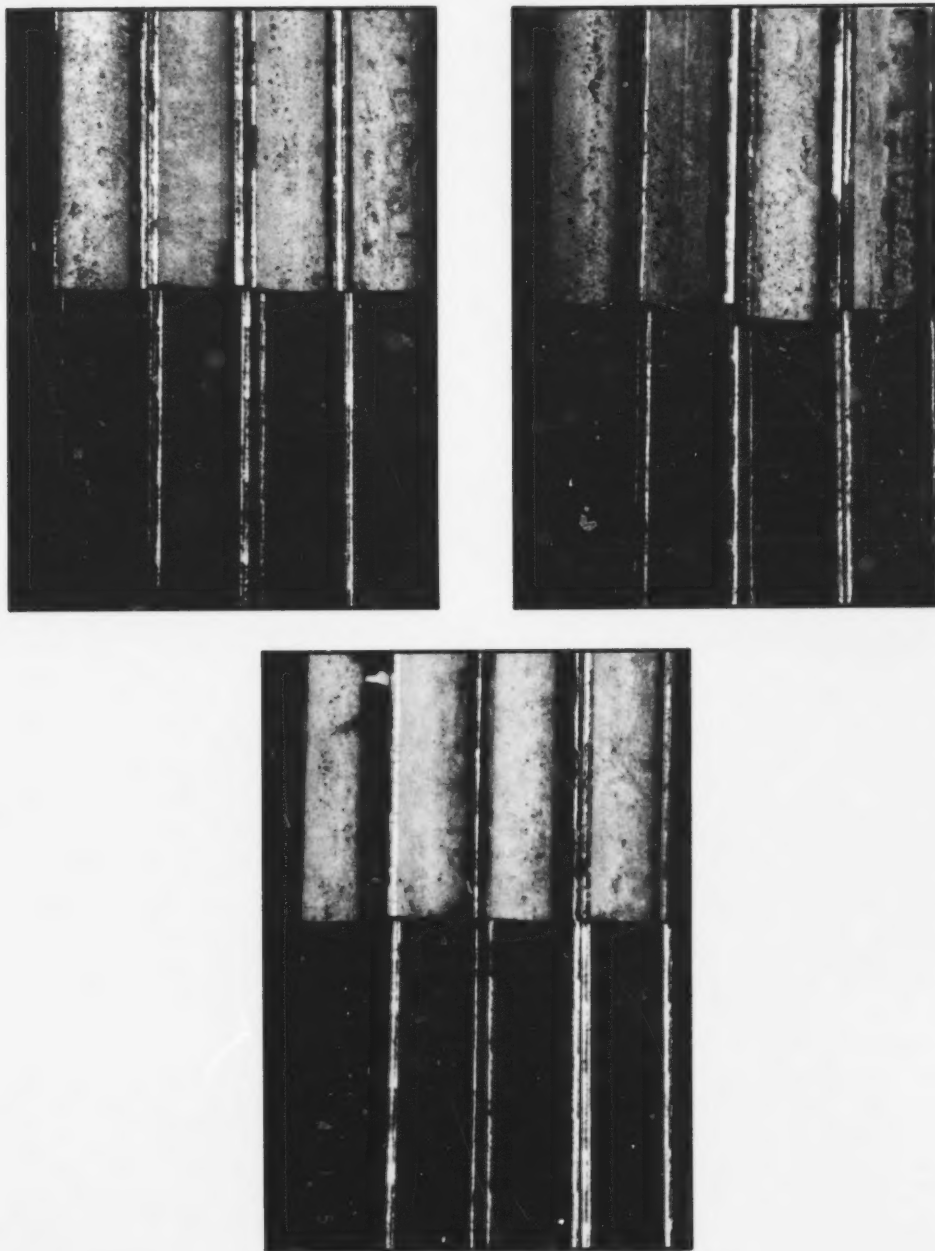


Figure 44. Pipe appearance, before and after cleaning, after 7 months exposure to SWP with 5.0 mg/L added copper. Clockwise from upper left: Australian pipe, Korean pipe and U.S. pipe.

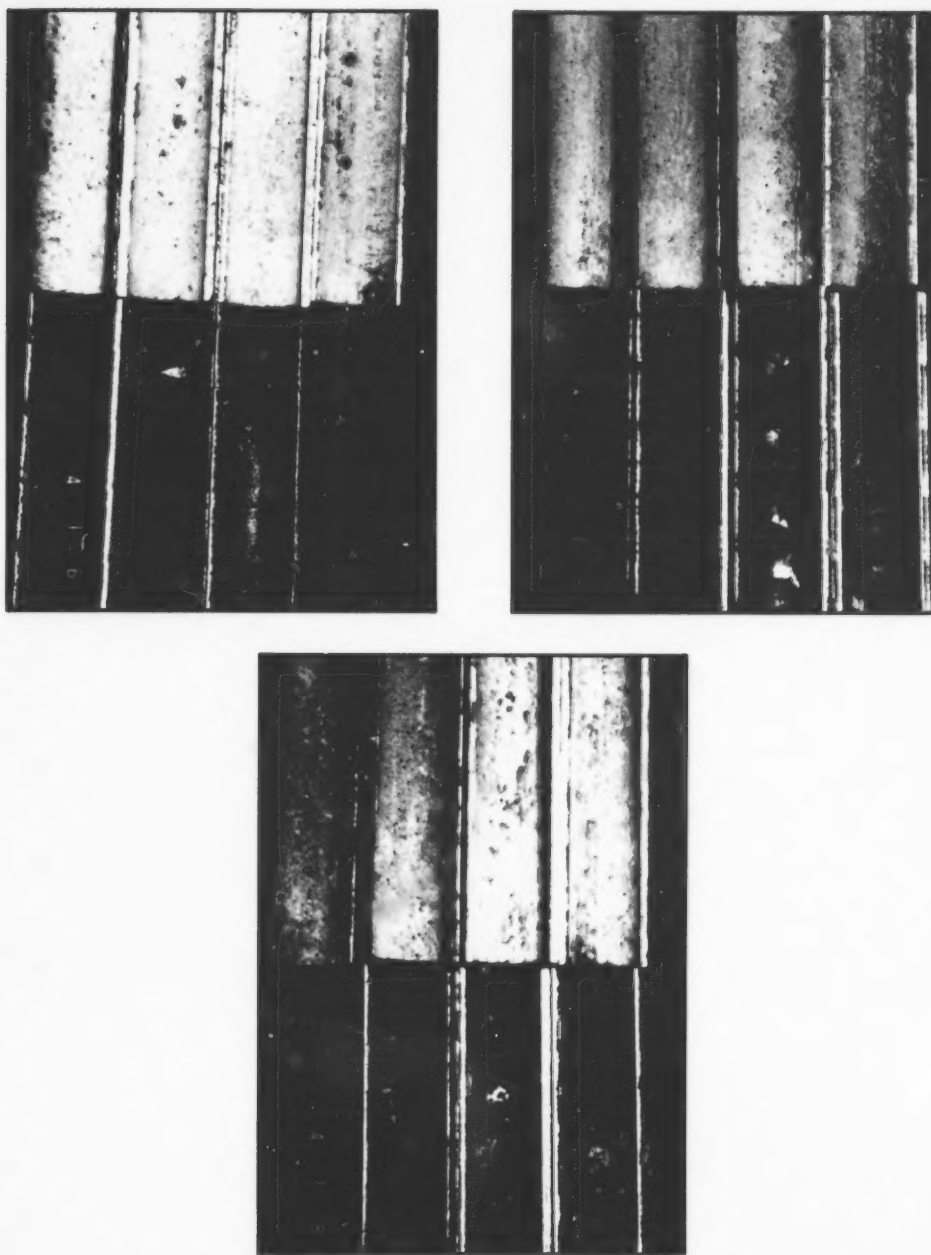


Figure 45. Pipe appearance, before and after cleaning, after 7 months exposure to SWP with 5.0 mg/L added copper and 2.5 mg/L added citrate. Clockwise from upper left: Australian pipe, Korean pipe and U.S. pipe.

### Scale Analyses - Colorado River Water Samples

Figure 46 shows the amount of scale buildup which occurred on pipes exposed to CRW and various copper doses for eight months and 20 months. In the intervening year, the amount of scale essentially doubled on the U.S. and Korean pipe samples, but showed no increase on the Australian samples. The amount of calcium deposited along the pipe surfaces again increased substantially on the Korean pipes, but showed essentially no increase on the U.S. and Australian samples (Figure 47). The amount of iron increased four to five times on the Korean and U.S. pipe samples (at the 5.0 mg/L copper dose), but again the Australian pipe showed no activity (Figure 48). The amount of zinc deposited increased on all three pipe types; the Korean pipe showed an eight-fold increase (1,000 mg/dm<sup>2</sup> to 8,000 mg/dm<sup>2</sup>), the U.S. showed a four-fold increase (1,300 mg/dm<sup>2</sup> to 5,000 mg/dm<sup>2</sup>), and the Australian showed a two-fold increase (1,500 mg/dm<sup>2</sup> to 3,000 mg/dm<sup>2</sup>) (Figure 49).

Copper also increased on all of the samples (Figure 50) but this reflects the pattern of copper addition and attrition. Essentially the eight month samples had been dosed with copper up through month five after which time the copper gradually leached away. The 20 month samples on the other hand had been dosed with copper for an additional five months (August through December 1983) and then had two months of leaching. Thus, Figure 50 shows no increase at 0.0 mg/L dose for all three pipe types, and a two-fold increase at the 1.0 and 5.0 mg/L copper dose levels.

The pattern of scale, calcium, iron, and zinc deposition is more significant in terms of corrosion. Essentially, the Korean pipe continued to show significant activity through month 20. Apparently zinc and iron were oxidized at anodic sites ( $\text{Zn} \rightarrow \text{Zn}^{++} + 2\text{e}^-$ ,  $\text{Fe} \rightarrow \text{Fe}^{++} + 2\text{e}^-$ ), and oxygen was reduced at cathodic sites ( $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ ) with resultant local increases in pH and calcium deposition. The U.S. pipe showed some additional corrosion activity and the Australian little or none.

These observations were borne out by conducting a two way analysis of variance test to determine the impact of pipe type (U.S., Korean and Australian) on scale deposition. The test indicated that at the 95 percent level, the amount of confidence level, the amount of calcium scale deposited was different for the three types of pipe and for the three copper doses.

### Scale Analyses - CRW and SWP Exposures

Figures 51 through 55 show results of pipe exposed to SWP water for seven months as compared to the eight month CRW samples. Overall, the SWP pipes showed less activity than the CRW pipes. For the total amount of scale, this difference (for the 5.0 mg/L Cu dose samples) was 1 to 2 gm/dm<sup>2</sup> greater for CRW. For calcium, however there is a 10-15 fold difference; the CRW samples range from 125-175 mg/dm<sup>2</sup> while the SWP samples range from 10-14 mg/dm<sup>2</sup>. For iron, the SWP samples range from 1.5-8 mg/dm<sup>2</sup> lower than their CRW counterparts. The zinc analyses follow a somewhat different pattern; for the U.S. pipes the amount of zinc on the surfaces is the same for both CRW and SWP samples. For the Korean samples, the CRW samples show less zinc deposited than the SWP samples; 600-800 mg/dm<sup>2</sup> less. The Australian pipes, on the other hand, show less zinc deposited on the SWP samples, 300-800 mg/dm<sup>2</sup> less.

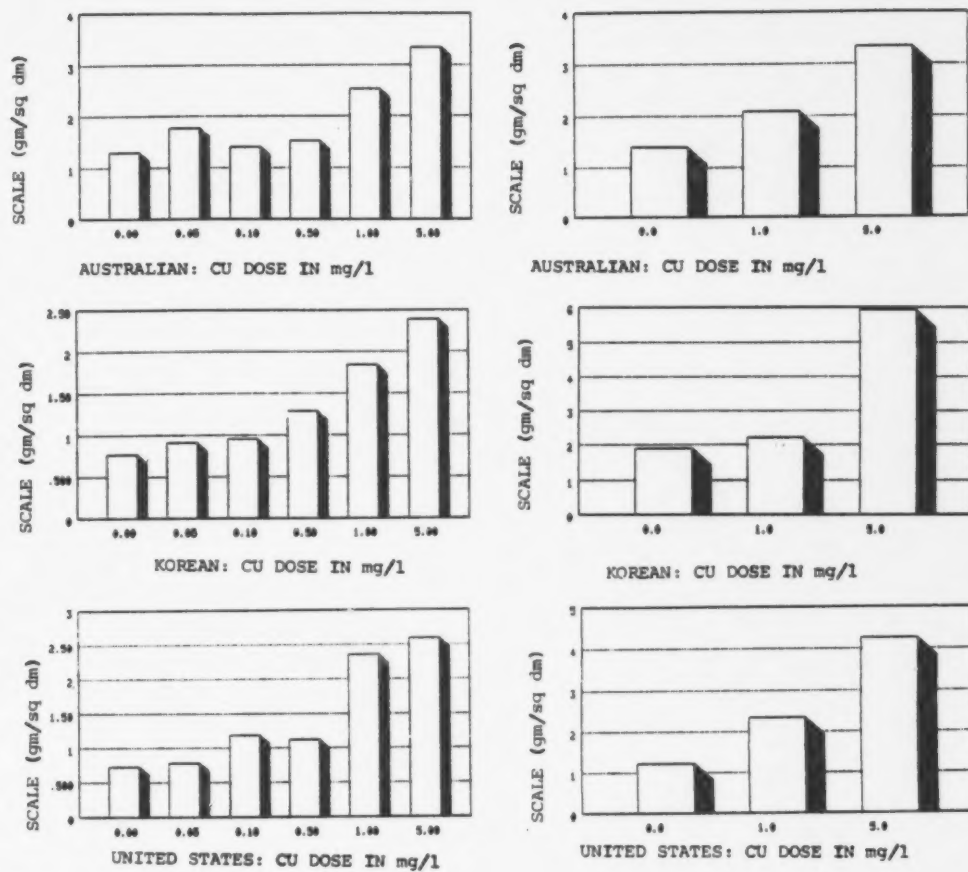


Figure 46. Scale deposition on test pipe exposed to CRW for 8 and 20 months.

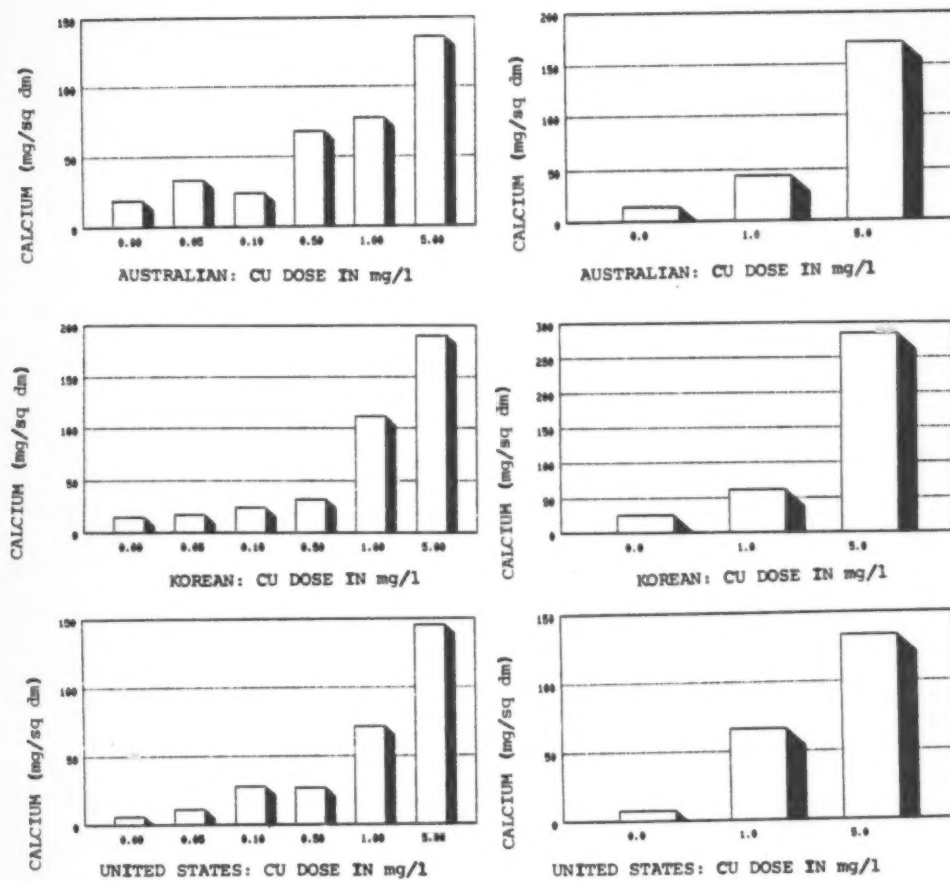


Figure 47. Calcium deposition on test pipe exposed to CRW for 8 and 20 months.



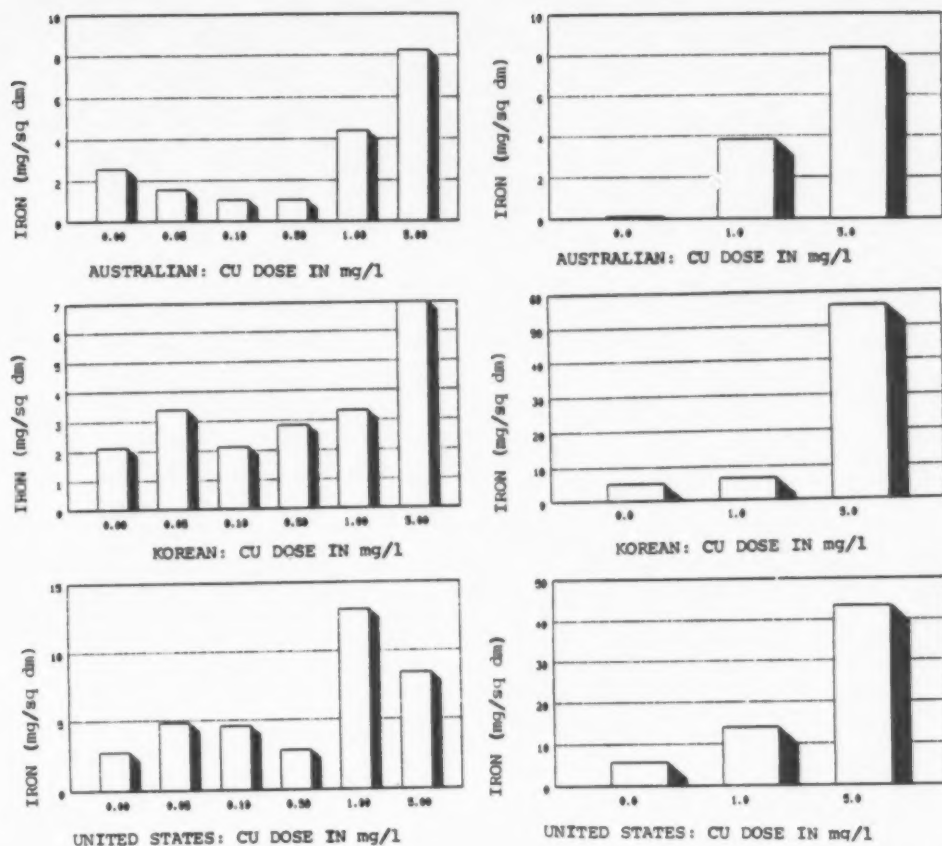


Figure 48. Iron deposition on test pipe exposed for 8 and 20 months.

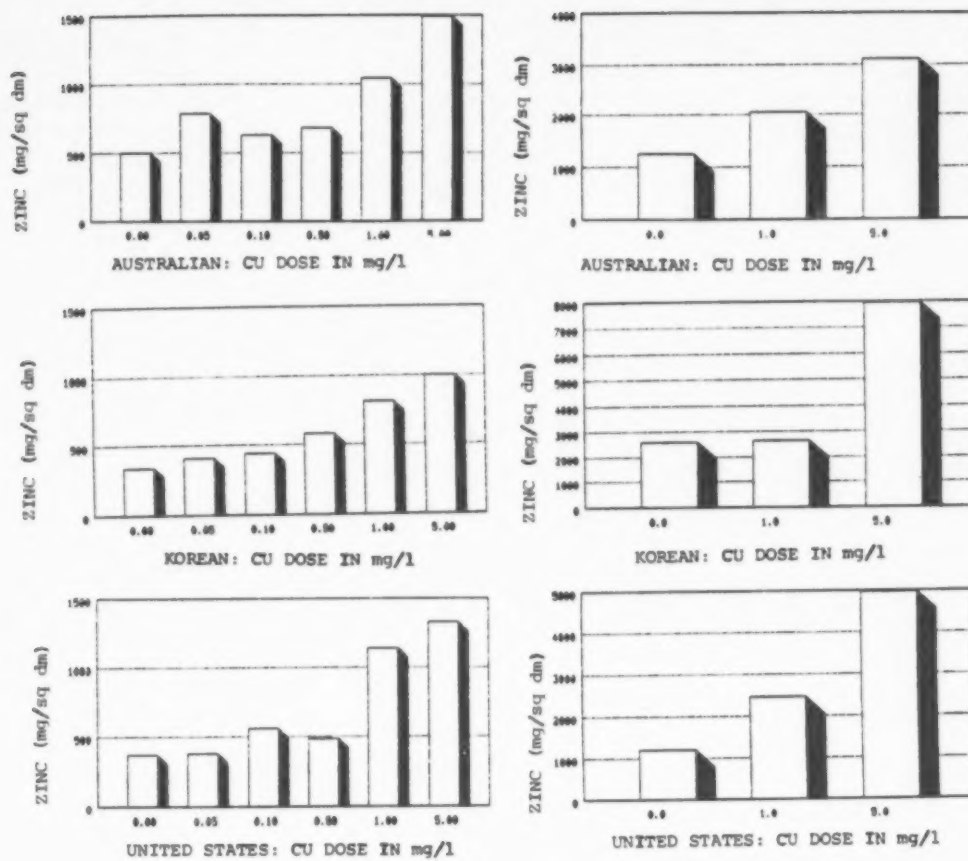


Figure 49. Zinc deposition on test pipe exposed to CRW for 8 and 20 months.

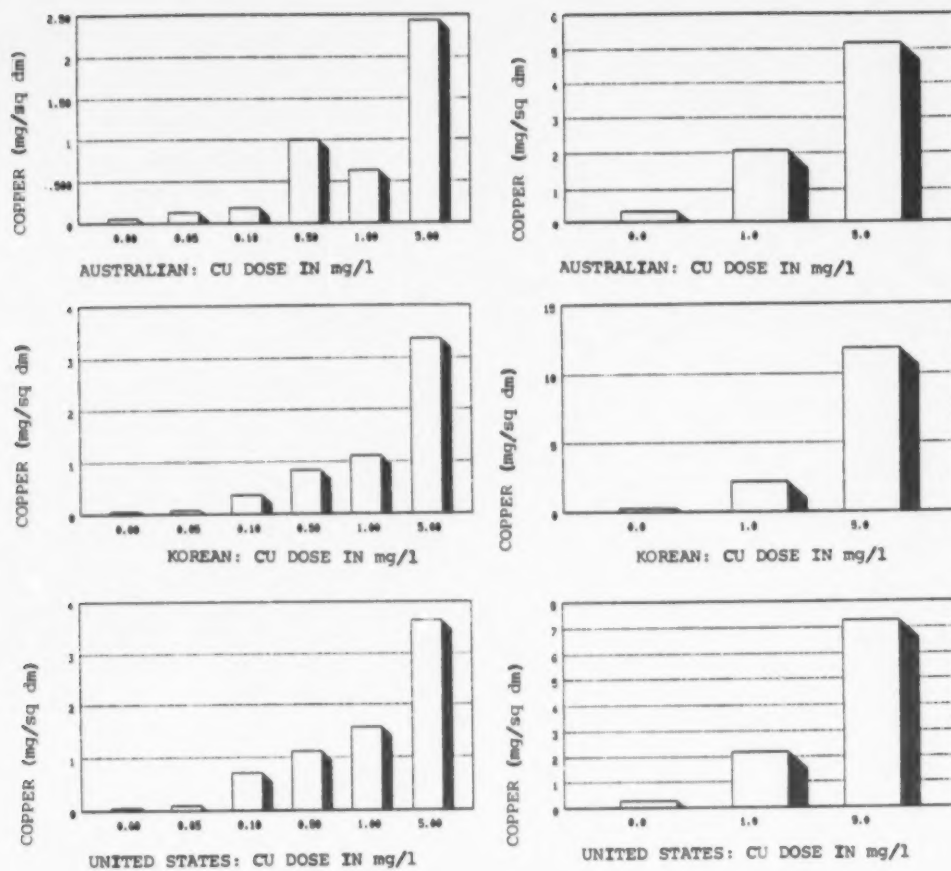


Figure 50. Copper deposition on test pipe exposed to CRW for 8 and 20 months.

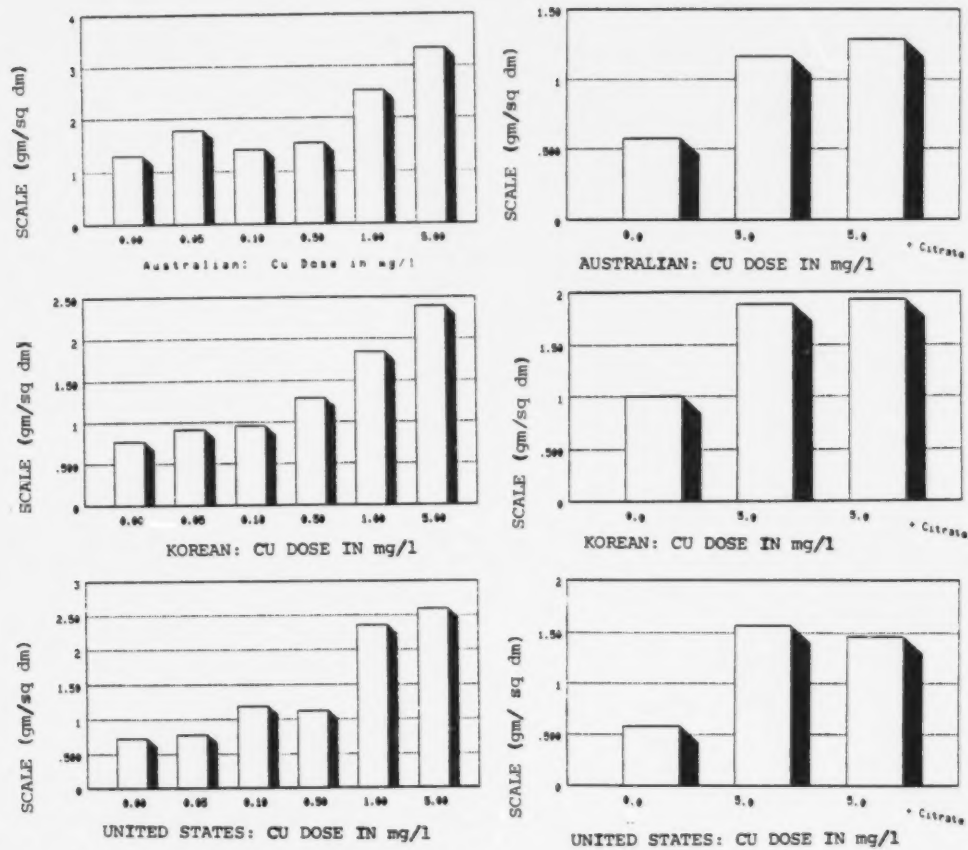


Figure 51. Scale deposition on test pipes exposed to CRW for 8 months (left) or SWP water for 7 months (right).

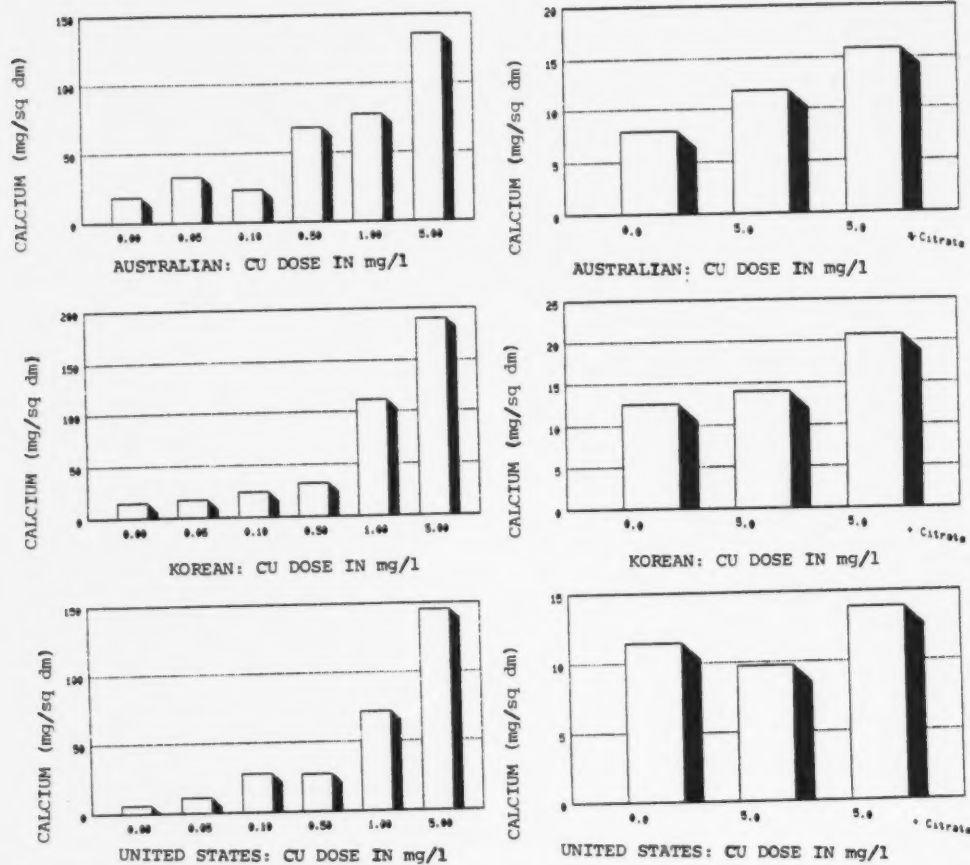


Figure 52. Calcium deposition on test pipe exposed to CRW for 8 months (left) or SWP water for 7 months (right).



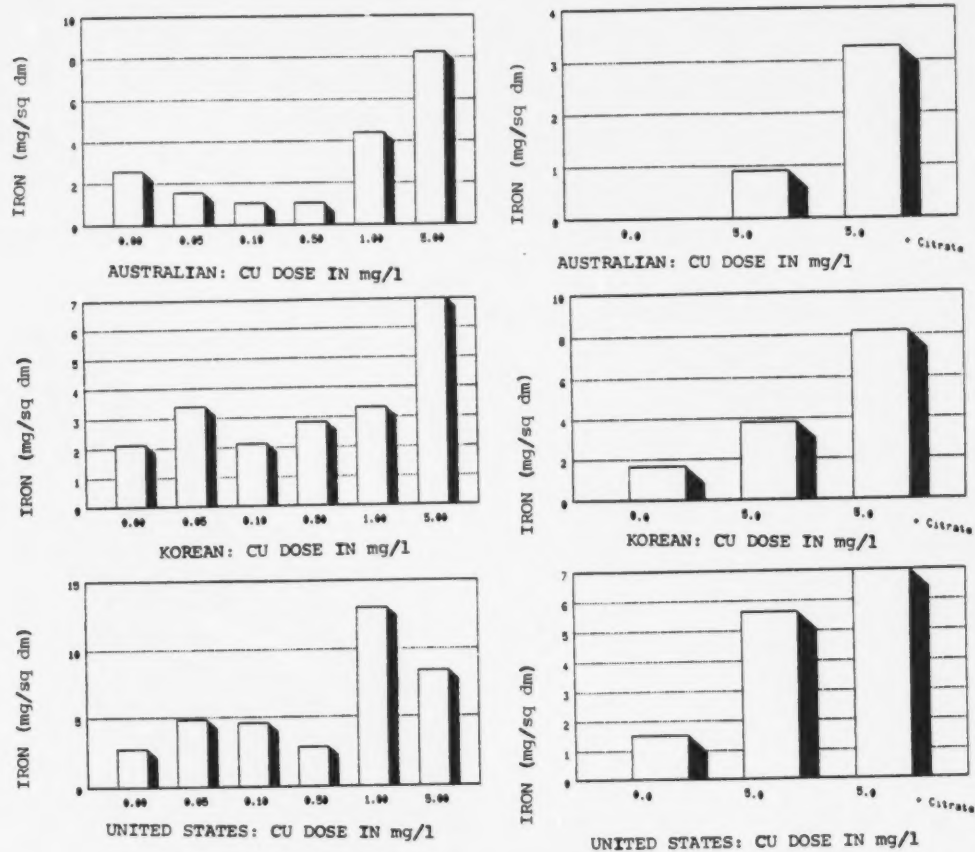


Figure 53. Iron deposition on test pipe exposed to CRW for 8 months (left) or SWP water for 7 months (right).

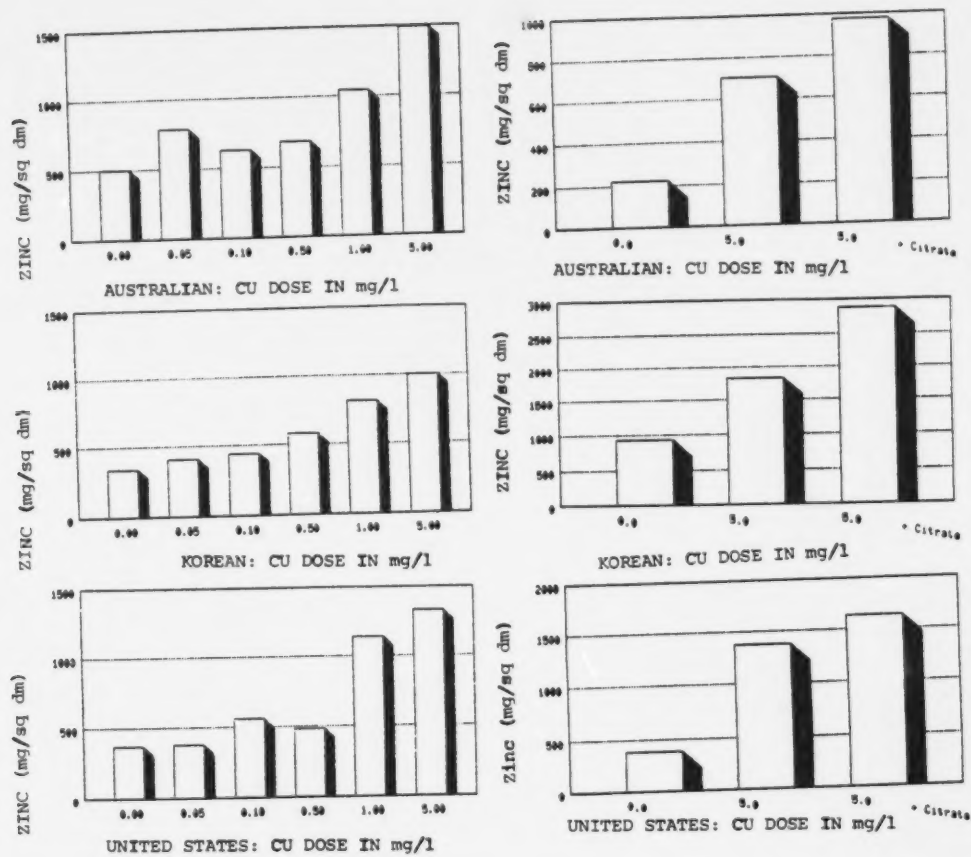


Figure 54. Zinc deposition on test pipe exposed to CRW for 8 months (left) or SWP water for 7 months (right).

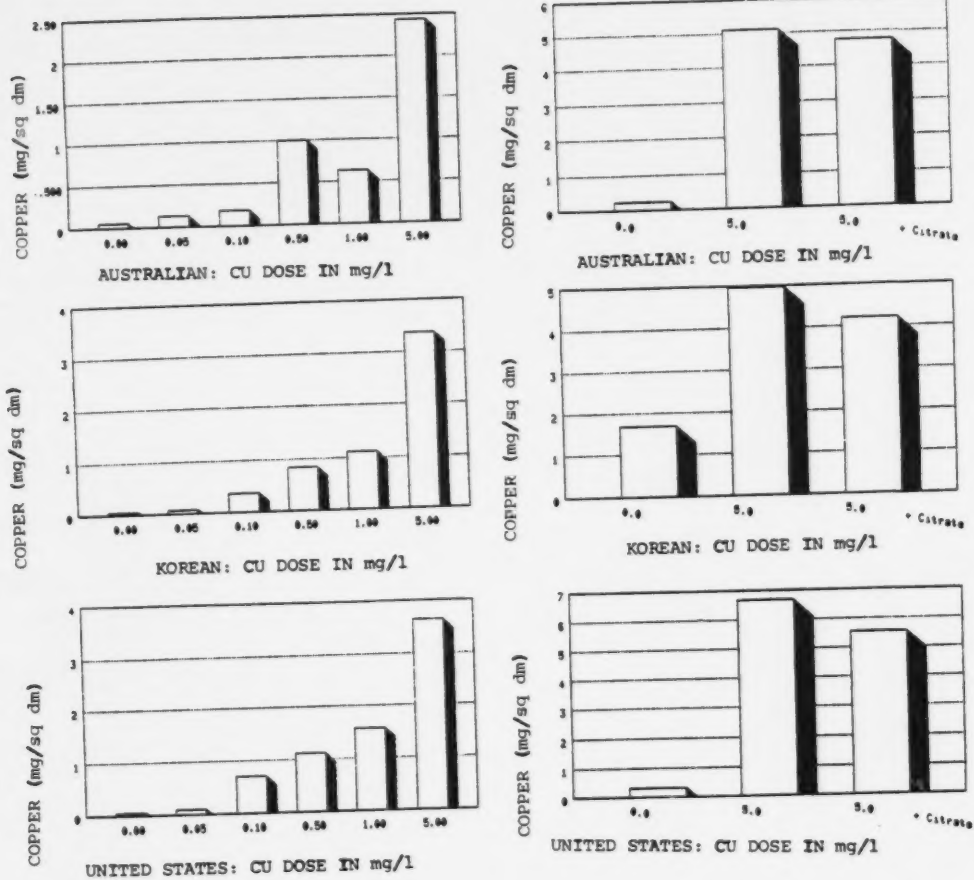


Figure 55. Copper deposition on test pipes exposed to CRW for 8 months (left) or SWP water for 7 months (right).

The pattern of copper deposition again reflects the pilot plant operational schedule, more copper occurs on the SWP samples because the months of addition had occurred recently.

The results for the scale and calcium buildup on the SWP pipes reflect the negative Langelier Index of SWP water, that is, a lower tendency to deposit  $\text{CaCO}_3$ . The lower amount of iron could reflect either a lower corrosion rate for the SWP pipes or a lesser amount remaining entrained on the pipe surfaces, because of the overall lower amount of scale present. The zinc does not follow any pattern; the U.S. SWP samples are the same as their CRW counterparts, the Korean are higher and the Australian are lower. This could suggest more corrosion occurring on the Korean pipes than on either the U.S. or the Australian, but the sample size is not large enough to draw any definite conclusions.

The citrated copper samples show overall more activity than the non-citrated copper. The difference in amount of scale deposited is not very noticeable, however there is a definite increase in the amount of calcium, zinc and iron deposited for the citrated versus non-citrated samples.

As stated in the beginning of this section, two "modes of exposure" were tested in the pilot test rack: one mode held the initial test water in the pipes for three months in a static condition before beginning the flow cycling, the other immediately began the flow cycling. The intent was to mimic the situation of new homes with little or no flow until after their sale.

A "paired t-test" was conducted on the resulting total scale, calcium, iron, and zinc deposition data to determine if a statistically significant difference occurred in the deposits on the pipes, resulting from the modes of exposure. The "paired t-test" showed that to the 95 percent confidence level, no significant difference existed between the deposition resulting from the two methods of exposure.

#### X-ray Fluorescence - CRW and SWP Exposures

X-ray fluorescence was used to determine the relative amounts of zinc and iron exposed on the pipe surface after scale removal. Increases in the extent of iron exposed at the expense of zinc removed would indicate greater corrosion activity. The ratio of iron to zinc surfaces, as a function of the added copper dose, the time of exposure, pipe manufacturer, and the source of water (either CRW or SWP), is presented in Figures 56 and 57.

As shown in both Figures 56 and 57, increasing copper doses led to increasing iron to zinc ratios, supporting the hypothesis that copper (or citrated copper) does speed the corrosion of galvanized steel pipe. Furthermore, the reaction occurs rather quickly, with the increase in exposure time to CRW from eight to 20 months not causing any measurable increase in the iron to zinc ratio. During the first seven months (SWP) or eight months (CRW) exposure, the large difference in water quality did not have an impact on the iron to zinc ratios. Over a longer period of time, the scaling tendency of CRW may cause reduced corrosion activity which does not occur with SWP.

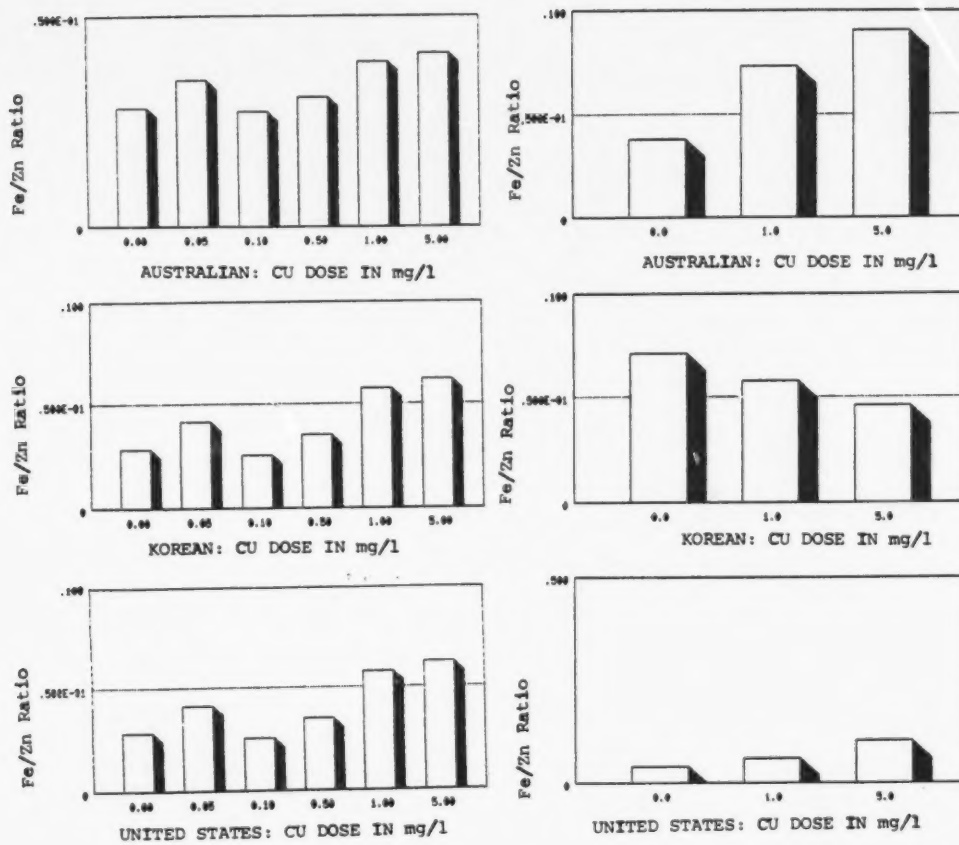


Figure 56. Fe/Zn by X-ray fluorescence ratios for 8 month and 20 month exposure to CRW.



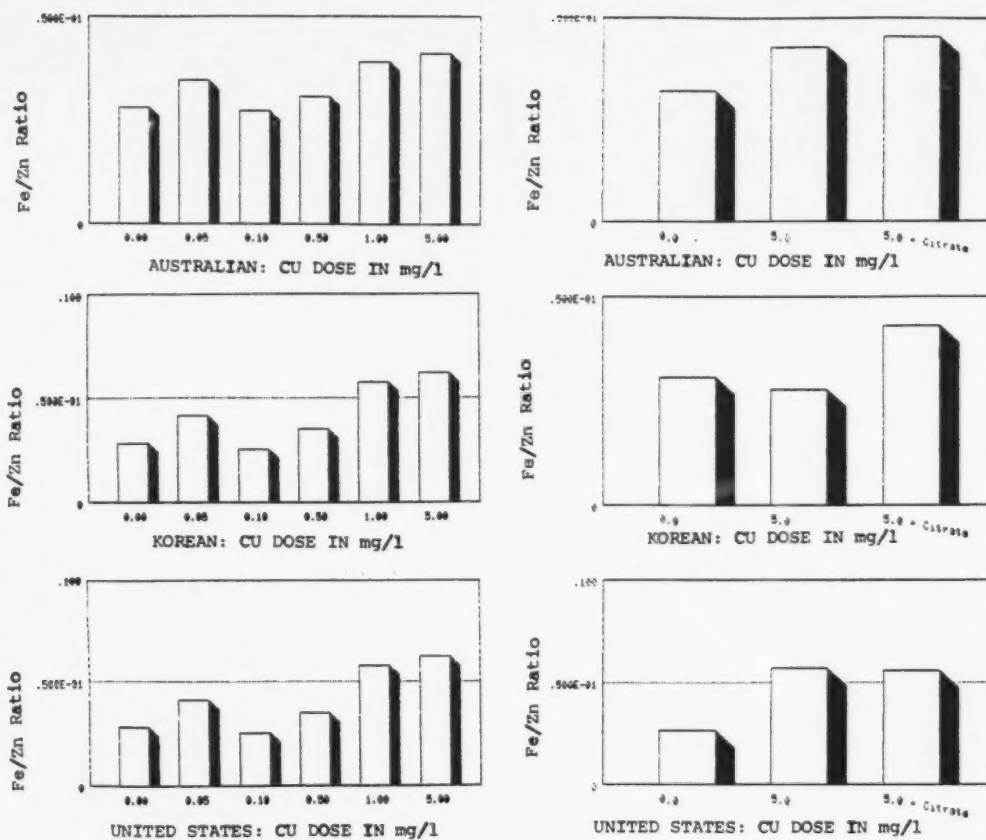


Figure 57. Fe/Zn ratios for X-ray fluorescence for 8 month CR7 exposures and 7 month SWP exposures.

Finally, the iron to zinc ratios were essentially in the range 0.04 to 0.06 for copper exposures from 1.0 to 5.0 mg/L for each of the pipe manufacturers. Very low copper doses (0.0 to 0.10 mg/L) produced iron to zinc ratios about half that large. Differences in manufacturing techniques did not appear to matter, nor did the addition of the citrate complexing agent.

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## APPENDIX A

### Hi-Rel Laboratories Report

MONTGOMERY CONSULTING ENGINEERS, INC.

Report Number MR-101136

#### INTRODUCTION

On October 27, 1981, Ms. Katherine Fox, of Montgomery Consulting Engineers, Inc., submitted three sections of galvanized steel pipe for analysis.

The objective of this analysis is to verify the composition of the various microstructural constituents of the zinc coating and to determine their thicknesses.

#### SAMPLE IDENTIFICATION

KP 2-2: Korean manufacturer  
AUS 2-1: Australian manufacturer  
USS 3-1: United States manufacturer

#### ANALYTICAL SEQUENCE

1. Metallographic Evaluation
2. Scanning Electron Microscope/Energy Dispersive X-Ray Analysis

#### METALLOGRAPHIC EVALUATION

One representative sample of each of the three manufacturers was vacuum encapsulated in epoxy and metallographically sectioned transverse to the long axis of the pipe sample. A calibrated filar eyepiece was used to determine the relative thicknesses of the zinc coating. This data is presented in Table I.



# SEM/EDXA

Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis techniques were used to determine the elemental composition of the various phases within the zinc coating.

The phases can be essentially characterized as a iron rich, zinc inter-metallic layer, an iron zinc diffusion zone and a relatively pure outer zinc layer. The data obtained is listed in Table II.

TABLE I  
DIMENSIONAL CHARACTERISTICS OF GALVANIZE LAYERS

|                                          | USS 3-1 |        | AUS 2-1 |        | KP2-2  |        |
|------------------------------------------|---------|--------|---------|--------|--------|--------|
|                                          | I.D     | O.D    | I.D     | O.D    | I.D    | O.D    |
| Overall Layer                            | .0037   | .0052  | .0029   | .0034  | .0027  | .0025  |
| Thickness (Min./Max.)                    | .0077   | .0041  | .0041   | .0053  | .0028  | .0026  |
| Fe-Zn Intermetallic                      | .00021  | .00012 | .00012  | .00007 | .00026 | .00026 |
| Thickness (Min./Max.)<br>Phase I         | .00090  | .0010  | .00040  | .00043 | .00047 | .00056 |
| Fe-Zn Diffusion Zone                     | .0007   | .00084 | .00075  | .0011  | .00075 | .00099 |
| Thickness (Min./Max.)<br>Phase 2         | .0019   | .0019  | .0029   | .0025  | .0017  | .0018  |
| Outer Zinc Surface                       | .0022   | .0042  | .00069  | .00056 | .0012  | .0008  |
| Coating Thickness (Min./Max.)<br>Phase 3 | .0034   | .0047  | .0025   | .0026  | .0017  | .0017  |

Note: All data listed as inches

TABLE II  
ELEMENTAL COMPOSITION OF PHASES

| Manufacturer | Phase I    | Phase 2    | Phase 3          |
|--------------|------------|------------|------------------|
| USS 3-1      | Zinc, Iron | Zinc, Iron | Zinc, Iron, Lead |
| AUS 2-1      | Zinc, Iron | Zinc, Iron | Zinc             |
| KP 2-2       | Zinc, Iron | Zinc, Iron | Zinc, Iron       |

#### ENGINEERING DISCUSSION

The presence of lead in the USS sample is typical because small amounts of lead are considered to be necessary for proper spangling. The absence of the element in the other samples raises some question as to the overall quality of these coatings.

In order to fully determine the most suitable coating for a particular application the base material should be analyzed as well, because differences in certain alloying elements or impurities can effect the coatings integrity.

Note: Spangling is the characteristic crystalline form in which a hot dipped zinc coating solidifies on steel strip

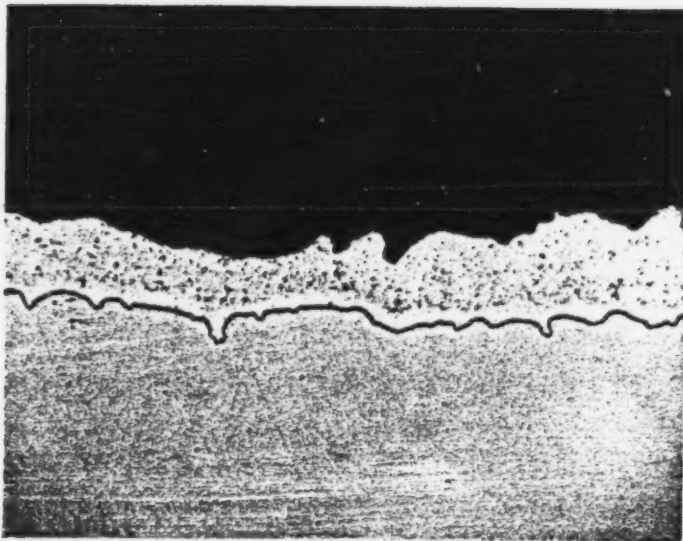


Figure 1. USS 3-1: Typical view of coating - inside diameter (85X).

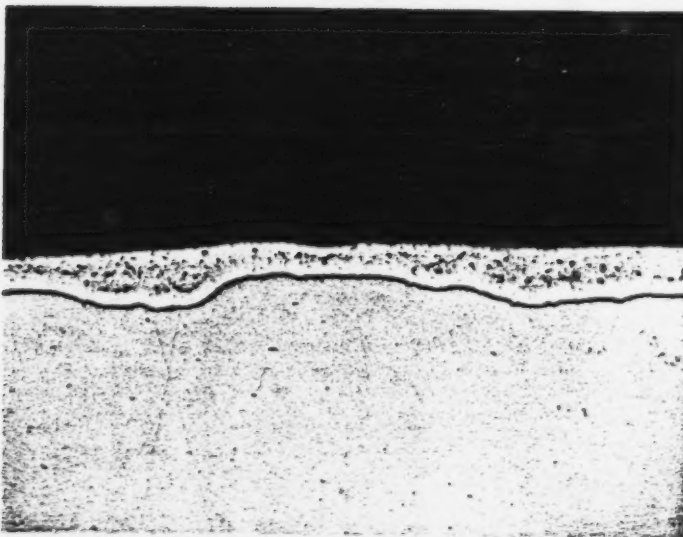


Figure 2. USS 3-1: Typical view of coating - outside diameter (85X).

Figure 3. USS 3-1: Higher magnification of coating - inside diameter (425X).

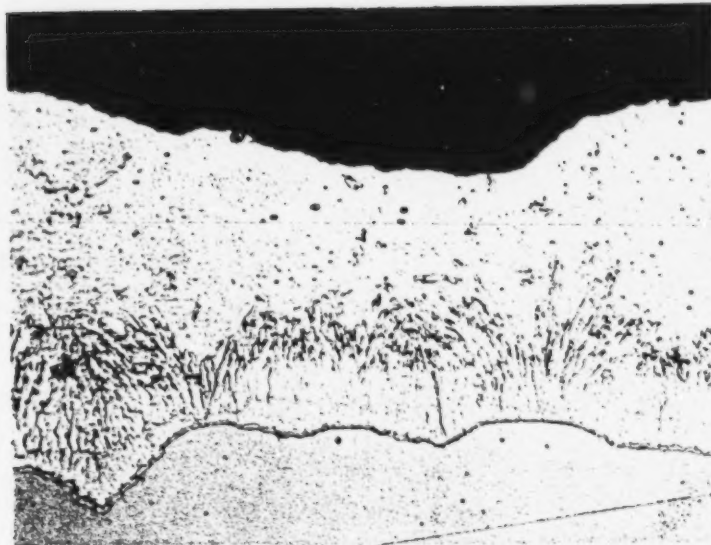
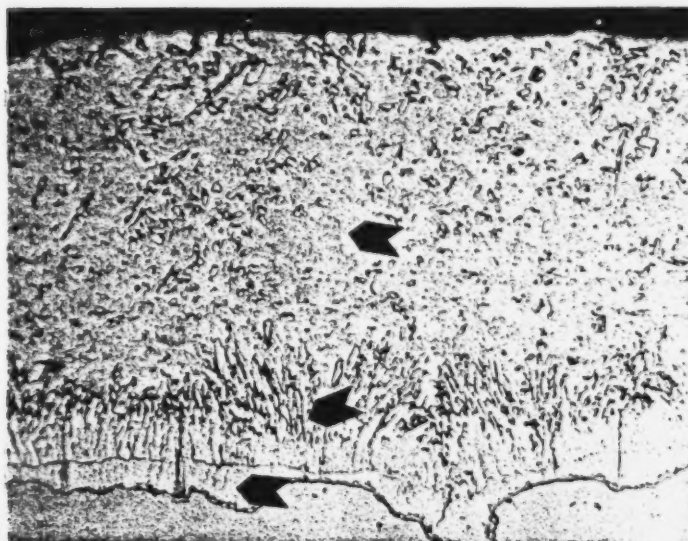


Figure 4. USS 3-1: Higher magnification of coating - outside diameter. Arrows indicate phases analyzed by EDXA (425X).



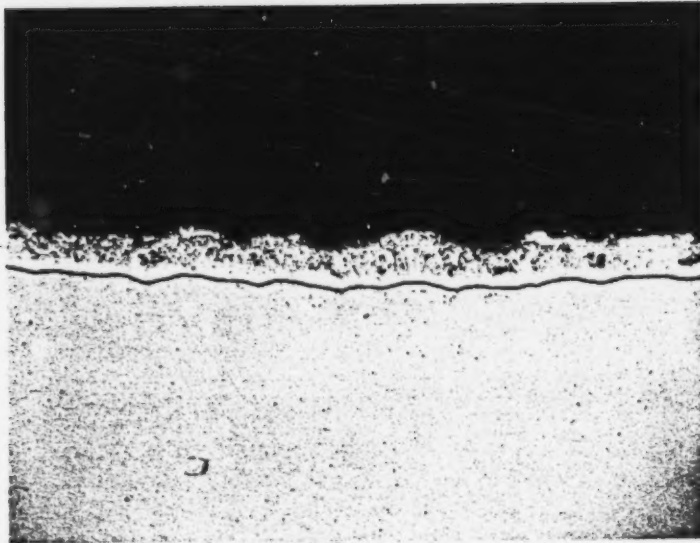


Figure 5. AUS 2-1: Typical view of coating - inside diameter (85X).

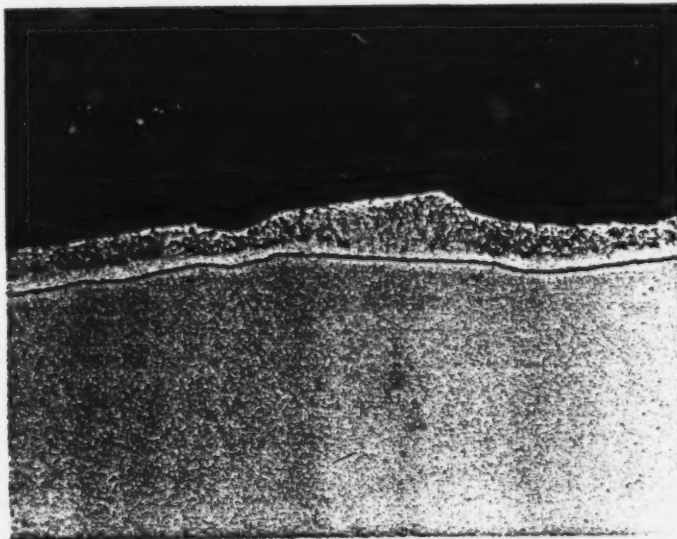


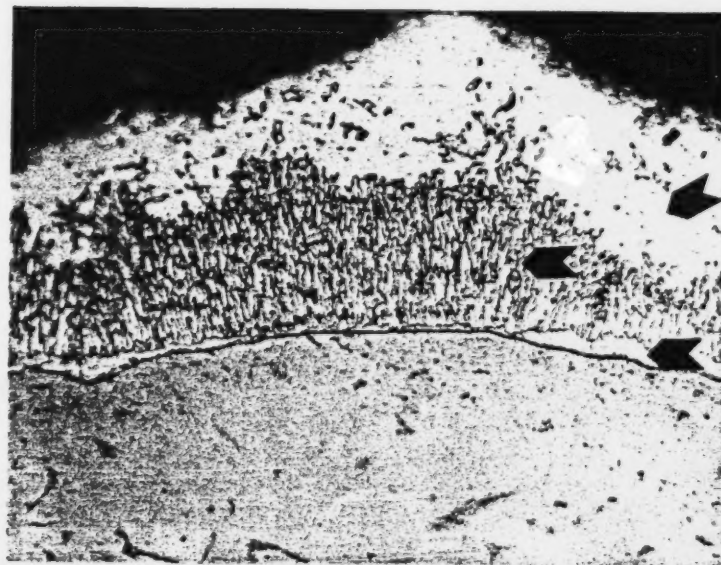
Figure 6. AUS 2-1: Typical view of coating - outside diameter (85X).



Figure 7. AUS 2-1: Higher magnification of coating - inside diameter (425X).



Figure 8. AUS 2-1: Higher magnification of coating - outside diameter. Arrows indicate phases analyzed by EDXA (425X).





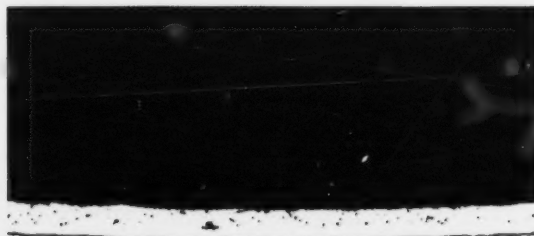


Figure 9. KP 2-2: Typical view of coating - inside diameter (85X).

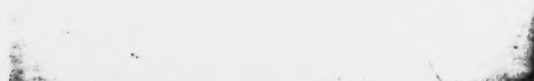


Figure 10. KP 2-2: Typical view of coating - outside diameter (85X).



Figure 11. KP 2-2: Overall view of burr found on the inside diameter of the tube (85X).

Figure 12. KP 2-2: Higher magnification of coating - inside diameter. Arrows indicate phases analyzed by EDXA (425X).

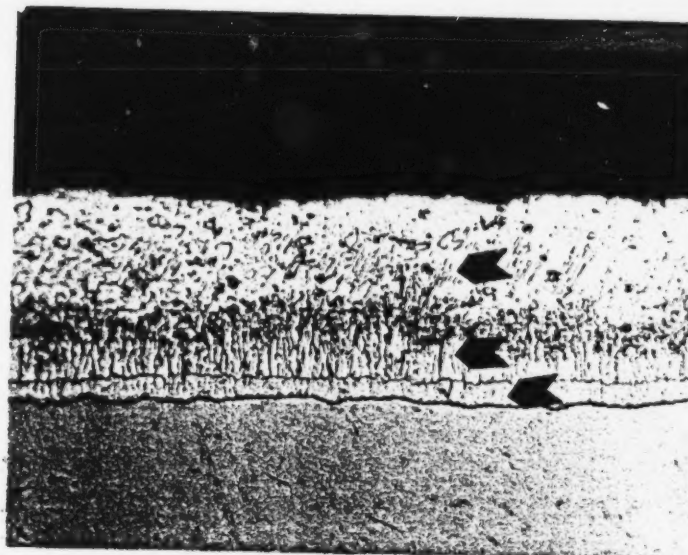
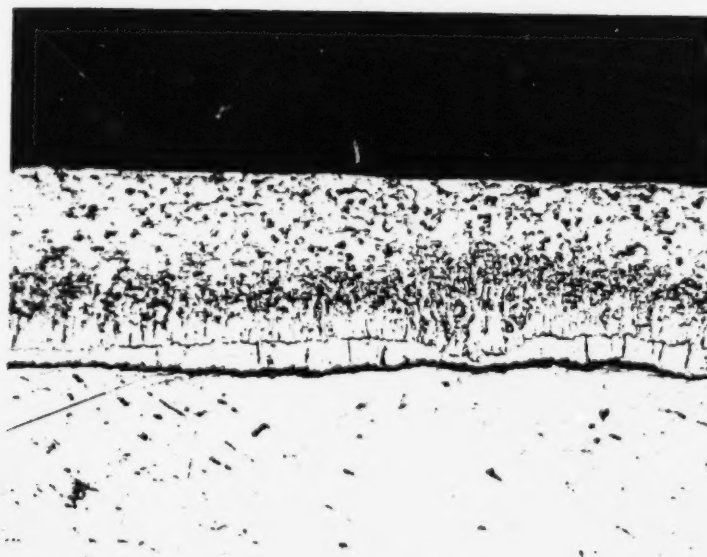


Figure 13. KP 2-2. Higher magnification of coating - outside diameter (425X).



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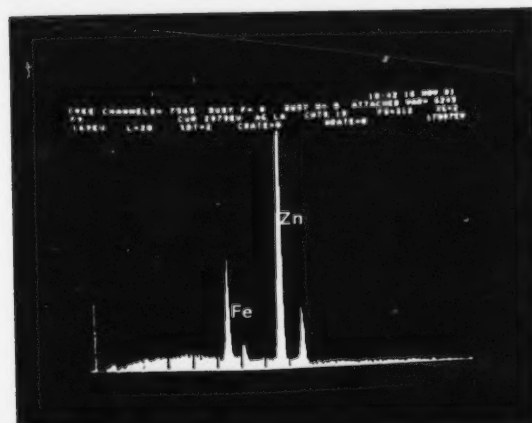


Figure 14. USS 3-1: Phase 1 EDXA spectra.

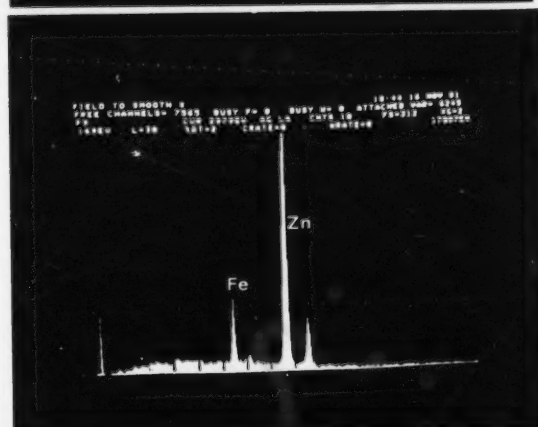


Figure 15. USS 3-1: Phase 2 EDXA spectra.

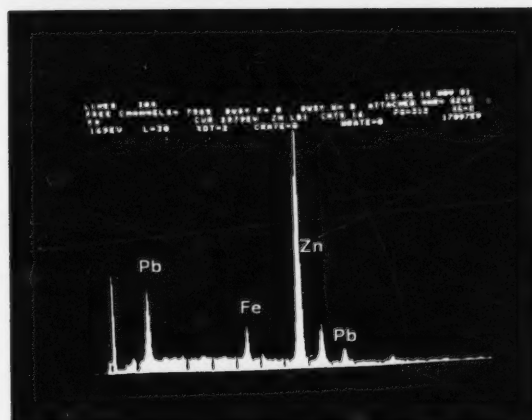


Figure 16. USS 3-1: Phase 3 EDXA spectra.

Figure 17. AUS 2-1: Phase 1  
EDXA spectra.

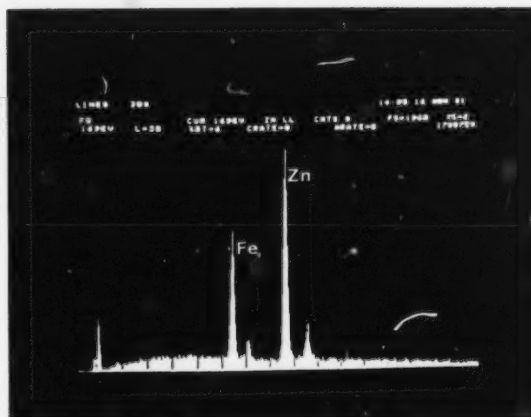


Figure 18. AUS 2-1: Phase 2  
EDXA spectra.

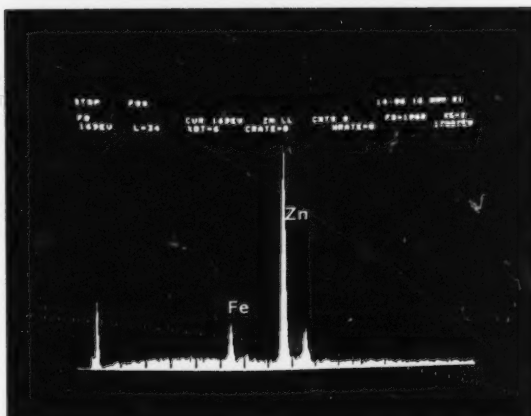
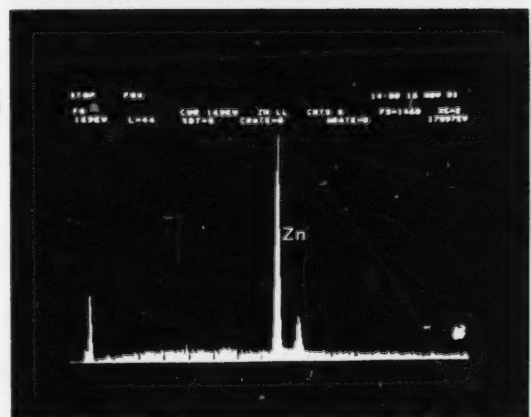


Figure 19. AUS 2-1: Phase 3  
EDXA spectra.



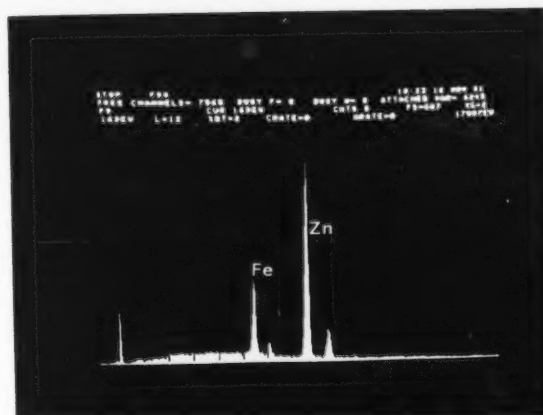


Figure 20. KP 2-2: Phase 1  
EDXA spectra

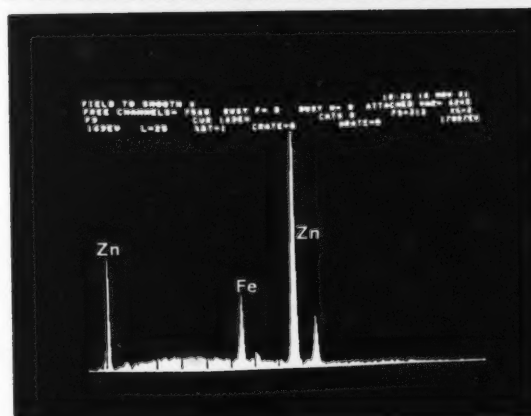


Figure 21. KP 2-2: Phase 2  
EDXA spectra.

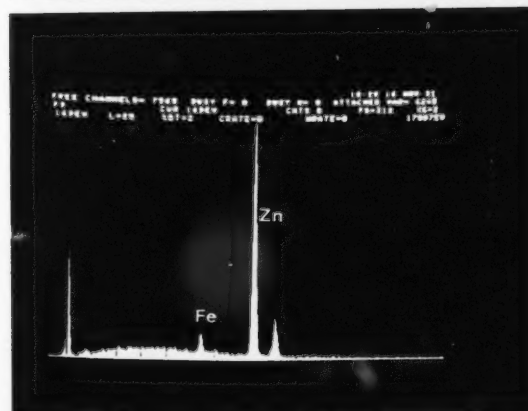


Figure 22. KP 2-2: Phase 3  
EDXA spectra.



## APPENDIX B

### Jerome F. Thomas Report

February 17, 1984

TO: James Montgomery Consulting Engineering, Inc.

FROM: Jerome F. Thomas

RE: Corrosion - Galvanized Pipe

The following facts including information contained in the attached report from Robert Lewis Ray, Metallurgical Engineer, are used to present an explanation for the enhanced corrosion problem that has developed in recent years in ordinary galvanized piping used in domestic, commercial and industrial potable water systems. It is significant to note that galvanized piping installed 20-30 years ago, in general, has not experienced similar corrosion failures.

1. Considering both material as well as installation in the overall cost, galvanized piping systems have become competitive with copper piping systems within the last fifteen years. Further, the occasional unavailability of copper has mandated the use of galvanized pipe. Mechanical engineers and architects have specified or allowed the use of galvanized pipe providing ASTM specifications have been met and the galvanized metal is electrically uncoupled by means of dielectric fittings from dissimilar metals. Contractors, because of economic considerations, will in general use the least expensive materials that meet the specification and codes.

2. There are three major manufacturers of galvanized pipe: Australia, USA and Korea. Korean manufactured galvanized pipe has been the least expensive available galvanized pipe in the last decade

and for this reason has essentially cornered the market with over 90% of new construction utilizing Korean Pipe. As indicated the corrosion problem in general has developed in approximately the last decade. However, construction specifying the use of USA piping has not experienced the corresponding corrosion problem. There is a strong indication that there is something unique associated with Korean pipe that is responsible for the enhanced corrosion.

3. Momentarily disregarding this latter strong indication, mention is made of a test conducted under the direction of J. Montgomery Engineers in the Los Angeles area. Copper was suspect as a possible initiator of the galvanized pipe corrosion. One source of the copper could be copper ions introduced in trace quantities in the surface supplies as copper sulfate for purposes of controlling algae. The copper ions in theory, would deposit on the surface of the galvanized pipe and being more noble would reduce back to copper metal. These micro/molecular deposits of copper would be point sources of corrosion cells drawing first zinc and ultimately iron into solution (corrosion). The localized corrosion debris, in the ensuing scenario, would initiate an oxygen differential type of corrosion which results in enhanced pitting type of corrosion, characteristic of the corrosion problem of galvanized pipe in recent years. In the test described in detail in a published paper ("The Interior Surface...", K. P. Fox, et al., Research and Tech., Feb., 1983, p. 84) copper ions were introduced under a variety of conditions into the three manufacture sources (Australia, USA and Korea). In summary, various copper concentrations, in hot water (140°F) were introduced for short periods in every hour except during the overnight period. After a period of many weeks a uniform coating was apparent on all pipes, but there was no evidence of the sever pitting type of corrosion characteristic of the problem of concern. Photographs of typical samples are shown in Figures 1-5, 17, 18, 19 in the Ray report.

4. Figures 1 and 2 are photographs of the interior surface of representative sample of unused (new) pipe and the corresponding exposed (used from J. Montgomery test). The captions on the figures are self explanatory. Of particular note is the welding seam readily

apparent on Korean pipe in Figure 2 and an apparent seam on the USA pipe. Figures 17, 18, 19 show cross sections of new pipes of the three manufacturers. What appears as a seam in the USA pipe in Figure 2 is not apparent in corresponding cross section. A fabrication technique has apparently eliminated weld seams in both Australian and USA pipe and annealing techniques have eliminated any discontinuities which would indicate the possible location of a weld seam. In contrast the interior weld seam of Korean pipe is readily apparent in cross section. In figure 14 the etched microstructure of new Korean pipe is shown at an amplification of 40x. More significant are the discontinuities at the weld flash which are considered detrimental to corrosion resistance (corresponding samples of Australian and USA pipes were searched for discontinuities at this amplification of 40x and none were found). The significance of this internal seam is indicative of one major difference in Korean pipe. The relationship to corrosion will be subsequently discussed.

5. One possible explanation for the relatively low cost of Korean pipe compared to Australian and USA pipe is a greater use of scrap steel in starting materials. However all manufacturers use scrap steel to various degrees and state-of-the-art technique requires that some amount always be used. Assuming scrap steel might contain a wide variety of trace contaminant metals including copper, analysis was run on the base metal of representative samples obtained from the Montgomery Engineers Test. The coatings were spalled off using a bending technique. Analyses were performed by emission spectroscopy on the spalled material as well as the base metal and the results are presented in tabular form in the Ray report. It is significant to note that the base metal from all three manufacturers contain approximately the same amount of copper which is present in small amounts (.02%; .02%; .03%) and probably controlled to these amounts to aid in the bonding of the zinc to the iron. The small amount of copper does not contribute to the corrosion problem.

It is interesting to note that the copper content of the spalled exposed coating showed a copper concentration in order of magnitude greater than the base metal (0.40%; 0.15%; 0.25%) obviously

contributed from the copper present in the hot, circulated test waters. There is no explanation of why the copper concentration is highest in the Korean pipe but it is interesting to note that every other cation contributed from the test waters is also present in highest concentration on the Korean pipe. The results were semiquantitatively checked by means of energy dispersive X-ray spectroscopy as shown in the Ray report. Although there is no explanation of why total cation concentrations including copper are higher on the Korean pipe, corrosion is more likely to occur in the presence of higher copper concentration.

6. The most significant point in the Ray report is indicated in Figures 9, 15 and 16 the microphotographs, 450X, of representative samples from the Montgomery Engineers test. In Figure 10 an interface abnormality is apparent between the base metal and zinc-iron alloy. In essence there is a discontinuity in the adhesion. This is apparent in both etched and unetched samples (Figures 9 and 10). The same discontinuity in adhesion is apparent in new Korean pipe compared to new pipe from the other manufacturers (Figures 11, 13, 12). The significance of this poor adhesion will be discussed as part of the scenario explaining corrosion pit formations.

7. The Montgomery Engineers Test did not demonstrate the typical type of corrosion which was the basis of the overall investigation. The explanation is that the tests were not of a long enough duration. As mentioned the hot water was circulated only for a small fraction of each hour except throughout the night period when there was no circulation. This flow pattern was used in an attempt to simulate typical household water use. In contrast it has been found in the Northern California area that the pitting type corrosion will occur in Korean pipe within a six month period in systems utilizing a circulating hot water loop (140°F). The water circulates 24 hours every day. The loop services individual apartments.

8. A number of representative corroded galvanized pipe samples, exhibiting the typical pitting type of corrosion were obtained from the Northern California area. (Captioned photographs are attached.)

These pipes were assumed to be Korean pipes as all exhibited an interior weld characteristic of Korean pipe. A typical example is clearly shown in Photographs A1 and A2. These samples were all obtained from hot water lines from large building complexes using continuously circulated loops at 135°F to 140°F. Some of the samples were obtained from failed, leaking pipes while others were removed from adjacent "working" pipe.

Photographs A1-A2 shows a sample from a pipe that had not yet failed. One half section has been cleaned showing numerous characteristic pits along the seam. The typical pits are found over the entire interior surface of the pipe but all failures were noted along the pipe seam.

Photographs B1 (corrosion debris removed) and B2 (corrosion debris intact) show an example of failure that has occurred along the pipe seam. The line in the photograph is not the raised weld bead. The weld bead has corroded away, and corrosion has proceeded into the weld seam following the discontinuities of the weld flash which can be observed in microphotographs of new Korean pipe as shown in Figure 14 of the Ray report (as mentioned, similar discontinuities could not be found in USA or Australian pipe). Note a small strip of paper that has been threaded through the failure and appears on both photographs. Multiple leaks have occasionally been observed on a single run of pipe all along the seam line. Photograph B-3 shows the interior side of the other half of this pipe (pencil points to position of corrosion failure). Every corrosion pit occurs under a tubercle mound. Many mounds have broken away and appear as oval red-brown cavities. The intact tubercle appears as a whitish mound (zinc hydroxy-carbonate is a white crystalline material). Observe the white oval spot in the upper left section of the photograph. Photographs B4, B5, B6 are progressive enlargements of this white spot located toward the center of the photographs. Photograph C-1 shows a tubercle partially broken. To further exemplify the tubercle mound or blister, cross sections were made of typical corroded pipe. Photographs D1, D2, D3, D4 and D5 show the pipe, and cross sections of both ends including enlargements. The cross sections cut through the blisters. The white edge of the



blister is zinc hydroxy-carbonate. The debris under the intact blisters is primarily black in color and corresponds to  $\text{Fe}_2\text{O}_3$ . The mechanism of this failure will be discussed under the heading entitled Scenario of Failure.

9. Figure 14 of the Ray report is a photograph showing the metal microstructure of new galvanized Korean pipe at the weld zone. The discontinuity under the bead continuing up through the seam is apparent under close scrutiny. The cavity under the weld bead is readily apparent. The mechanism of failure along the weld bead is related to but slightly different from that occurring under areas of galvanizing away from the welding seam. This mechanism will also be discussed under the heading Scenario of Failure. Comparable photographs of cross sections of new pipe of Korean, USA and Australian manufacture are shown in Figures 17, 18, and 19 of the Ray report. The weld bead and discontinuities under the bead apparent in Korean pipe cannot be found even under close microscopic scrutiny in USA and Australian pipe.

10. The ASTM Standard Specifications - Designation A 120-81, 2.1-A90 Test for Weight of Coating and 17.2 The zinc coating on galvanized pipe shall be free of voids or excessive roughness are the specifications relating to galvanizing. Comparable adherence tests for galvanizing on hardware, ASTM Standard Specification - Designation A 153-82, 5.5 The zinc coating shall adhere tenaciously to the surface of the base metal (stout knife test and pivoted hammer test), are not included in pipe specifications.

11. A brief review of the galvanized pipe manufacturing process indicates a possible explanation for the basic cause of the corrosion problem associated with galvanized pipe. In summary, a long, narrow coil strip of steel called a skelp is fed into a furnace and at very high temperatures is rolled into a tubular form with the edges butting to form a continuous tube or pipe. A weld is produced at the butt. An air blast is used to remove mill scale prior to making the butt weld. Stretching and rolling at high temperature eliminates the external weld bead and reduces the diameter and wall thickness to

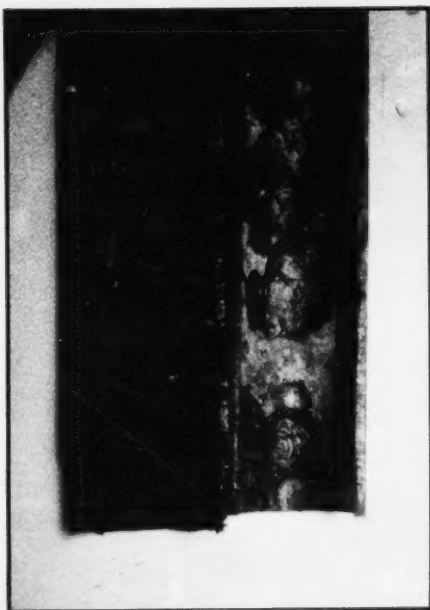
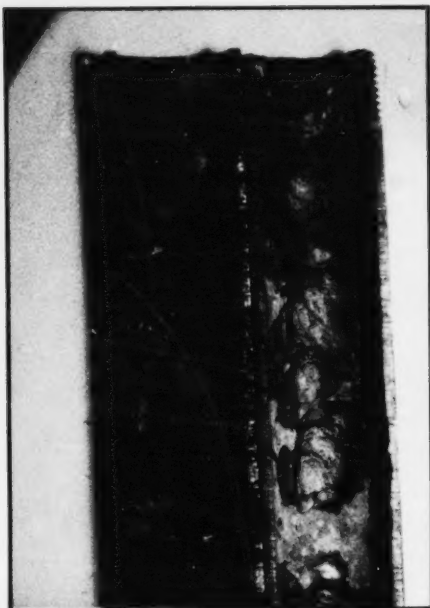


approximate size. The continuous pipe is cut to desired lengths and at a sizing mill is brought to exact size, possibly reamed, annealed and cooled for galvanizing operations. USA and Australia use a thermal weld whereas Korea uses an electroinductive welding technique. To minimize electrical resistance at the seam a much higher pressure is used in the electroinductive weld resulting in an inner and outer weld seam. The outer weld is removed at the sizing mill but the inner weld seam remains. The mill scale is removed by an acid bath, followed by washing and neutralizing baths. The hot pipe is then introduced into a flux bath prior to being dipped into a molten bath of zinc. The pipe may be rotated at an angle to drain and uniformly coat. Steam or air may be passed through the pipe as an aid to uniform coating. Many factors may affect the quality of the galvanic bond: The elemental composition of both the base metal and the zinc; the effectiveness of removing mill scale both by air blast and acid blast; the effectiveness of wash solution and neutralizing solution, both wetting and removing (the acid, wash and neutralizing steps are significant in pipes having an interior weld bead with the inherent crevice under the bead.); the effectiveness of the flux bath; the residence time, temperature of the various baths including the molten zinc and the temperature of the base metals in the baths all affect adhesiveness and cohesiveness. The production of the proper amalgams between the base metal and the exterior zinc coat is very significant.

12. Scenario of Failure - The essence is to develop a zinc-hydroxy carbonate semipermeable membrane over the base steel metal of the pipe. Any more noble soluble element in the circulating water such as copper iron will be very effective at developing the membrane; a uniform coating of this noble metal would be most effective but a random distribution would be effective if the metal ion deposited in a critical location. A critical location is a spot at which there is poor adhesion of the zinc to the base metal. Perfect adhesion is an unobtainable objective of all manufacturers, however, there is a strong indication that Korean pipe exhibits a lesser degree of good adhesion than the norm. Noble metal ions are most effective in that they continue to oxidize the zinc indefinitely after deposition which is an essential precursor to forming the insoluble zinc

hydroxy-carbonate. The dissolved oxygen in the water can also form the zinc-hydroxy carbonate membrane but at a slower rate. If acid, caustic, or even rinse water is trapped under the welding bead, which is only possible with Korean pipe, the zinc will corrode from an internal mode but again developing the porous zinc membrane. Temperature is also significant effecting oxidation rates and solubility of the zinc salt; the higher the temperature the faster the rate and the less soluble the zinc salt. The zinc membrane corresponds to a mound of corrosion debris on the base metal. The next step, as in any corrosion scenario, is the oxygen differential or concentration cell. The base metal corrosion products occupying a greater volume than the base metal will cause the zinc membrane to "blister" and ultimately break. The total dissolved solids in the water phase is also significant, contributing to the conductivity of the internal circuit; for example the conductivity of Los Angeles water is much greater at a TDS of 500-700 ppm compared to the San Francisco Bay Area water with a TDS of 50 ppm. The cell of this internal circuit consists of the base iron metal as the cathode and any adjacent zinc metal having good adhesion to the base metal serving as the sacrificial anode. The more conductive the aqueous phase the further the reach of the sacrificial anode. Thus the corrosion typical of galvanic piping in recent years should occur more readily in the Northern California area.

13. Why hasn't the galvanized piping in the J. Montgomery test failed in the characteristic pitting fashion? It has actually started and eventually would have appeared similar to the pitting corrosion exemplified in Photographs A, B, C and D. Figures 1 and 2 in the Ray report are photographs of representative halves of new and used (from the J. Montgomery test) piping. Figures 3, 4 and 5 are microphotographs (25x) of the used piping. Figure 3 shows the definite start of the zinc blisters on Korean pipe. Figure 5 shows the start of zinc blisters to a much less degree on USA pipe. Figure 4, the corresponding photograph of Australian pipe, does not indicate the presence of any blisters. If the hot water had been allowed to circulate continuously the corrosion would have become readily apparent in a short period.



Photographs (clockwise from lower left). A1. Galvanized pipe from recirculating hot water system. A2. Same. B1. Failure of galvanized pipe in recirculating hot water system (pipe interior). B2. Same (pipe exterior).



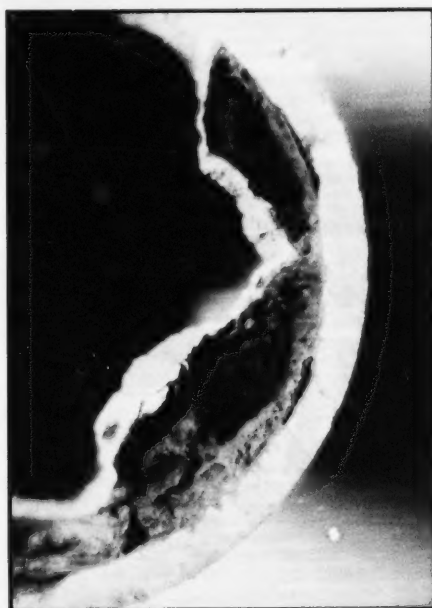
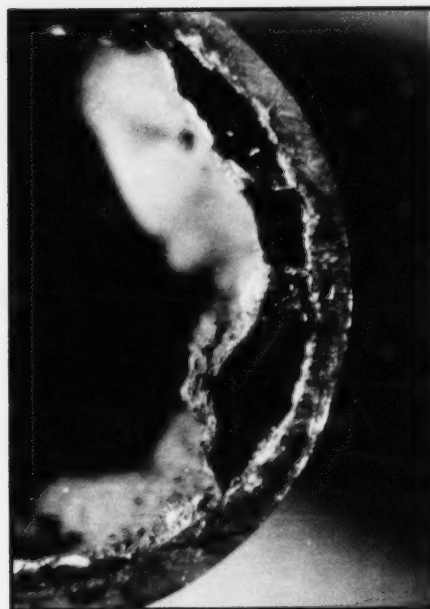
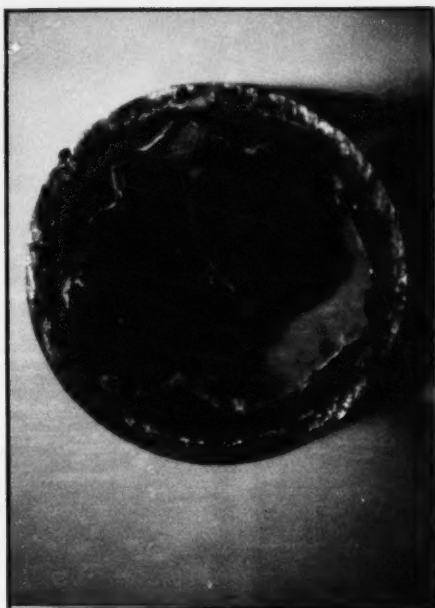
Photographs (clockwise from lower left) B3.  
Failure of galvanized pipe in recirculating hot  
water system (pipe interior). B4, B5, B6.  
Progressive enlargements of white mounded material  
seen in upper left corner of B3.





Photographs (clockwise from upper left). C1. Broken tubercle from galvanized pipe in recirculating hot water system. D1. Exterior of galvanized pipe in recirculating hot water system. D2. Cross-section of galvanized pipe in recirculating hot water system.





Photographs (clockwise from bottom left). D3, D4, D5. Cross-sections of galvanized pipe in recirculating hot water system.

APPENDIX C

Robert Lewis Ray, Inc., Report

February 8, 1984

3-1014M

J. F. Thomas, Ph.D.  
University of California  
Department of Sanitary and  
Environmental Engineering  
Davis Hall  
Berkeley, California 94720

RE: Corrosion Study, MWDSC  
J. S. Montgomery Engineers  
Galvanized Steel Water Pipe

Dear Professor Thomas:

Following your instructions, I have studied 3/4" IPS galvanized steel water pipe which you furnished, as follows:

I. Exposed (Used) Pipe Samples, Water Flow:

- . 5 months added Cu dosage 5 mg/l 50 minutes per day, 4 days per month
- . 3 months subsequent, water only

Longitudinal half-pipe sections

K (Korean) K337

A (Australian) A4826

U (United States) US100

II. Unexposed ("New") Pipe Samples

Longitudinal (Half) sections

Full Pipe sections

The purpose of my work was to determine the nature of the corrosion effects (coating and base metal) for the exposed specimens and to compare the effects with the base metal manufacture (K, A, U).

### Test Procedures and Results

#### A. Visual Examinations

The specimens were examined by eye and under the bench stereomicroscope to 30X.

##### 1. Exposed Samples (K, A, U)

Corrosion effects were quite similar in visual appearance for the three specimens as illustrated, Figure 1. Sample K appeared to have a weld seam, but there were no distinctive corrosion products in evidence by this examination. However, galvanized coating roughness, ridges, and other surface irregularities varied, all illustrated in the photographs (Figures 1 and 2). The corrosion coatings appear to be somewhat tenacious, with thickness of .003" - .005". Small particles with shiny metallic lustres were observed interspersed in the coating matrices, under the stereomicroscope. These were later studied under the scanning electron microscope and found to be Fe shavings, introduced by section sawcuts. Photomacrographs at 25X show the details of the compound formation on the galvanized coatings, Figures 3, 4, and 5.

##### 2. Unexposed Pipe Samples (K, A, U)

The irregularities in surface appearance varied between the three samples, as noted, Figure 2.

#### B. Chemistry, Galvanized Pipe

Chemical analyses on each exposed pipe sample were conducted by emission spectroscopy. The spectroscopy was conducted at .020"-.025" depth below the I.D. surfaces.

Chemical Compositions MWD Galvanized Pipe

| Base Metal, Exposed Samples |         |         |         |
|-----------------------------|---------|---------|---------|
| Element                     | K       | A       | US      |
| C                           | .03%    | .12%    | .14%    |
| Mn                          | .35%    | .46     | .42     |
| P                           | .014    | .029    | .008    |
| S                           | .016    | .035    | .020    |
| Si                          | .006    | .02     | < .005  |
| Cu                          | .02     | .02     | .03     |
| Cr                          | .01     | .01     | .05     |
| Ni                          | .02     | .01     | .01     |
| Mo                          | < .005  | < .005  | .005    |
| Al                          | .03     | .007    | < .005  |
| V                           | < .005  | < .005  | < .005  |
| B                           | < .0005 | < .0005 | < .0005 |
| Fe                          |         | Base    |         |

Noteworthy features of the above analytical results are suggested:

1. Each sample is relatively low in copper, the element utilized as an additive in the test water makeup. The low amounts of copper and equivalent Cu results indicate that the Cu content in the pipe composition is probably not a variable in the study.
2. The K (Korean) pipe has considerably lower carbon than the A (Australian) and US (United States) manufacture. This variation in the compositions is not considered significant in relation to corrosion effects.
3. Other variations in the quantities of metallic elements are also not considered significant in relation to the corrosion study.

C. Chemistry, Corrosion Products (Coatings), Spectroscopy

Specimens were taken from each exposed pipe sample by spalling the coatings free from their sub-strates, utilizing a bending (deformation) technique. Emission spectroscopy and "wet" chemistry were then conducted to obtain the "bulk" coating composition.

Chemical Compositions, Corrosion Coatings, Exposed Pipe

Spectroscopy

|    | K       | A       | US      |
|----|---------|---------|---------|
|    | Major % | Major % | Major % |
| Zn | 5.0     | 3.0     | 1.0     |
| Ca | 1.5     | 1.5     | 1.5     |
| Al | 1.0     | .80     | .30     |
| Cu | .40     | .15     | .25     |
| Mg | .30     | .30     | .15     |
| Fe | .18     | .14     | .16     |
| Pb | .08     | .10     | .08     |
| Mn | .03     | .009    | .009    |
| Sr | .02     | .01     | .002    |
| Ba | .03     | .02     | .02     |
| Ki | .01     | .01     | .01     |
| Ti | .008    | .002    | .002    |
| Cd | < .005  | < .005  | < .005  |
| Sn | .004    | .02     | .004    |
| Cr | .002    | < .001  | .002    |
| Ni | .001    | < .001  | < .001  |
| Bi | .0008   | .0008   | .0008   |
| Ag | .0002   | .001    | .0002   |



Chemical Compositions, Corrosion Coatings, Exposed Pipe (Cont'd.)

Wet Chemistry

|                 | K     | A     | US    |
|-----------------|-------|-------|-------|
| CO <sub>3</sub> | Major | Major | Major |
| S (total)       | .5%   | .6%   | .8%   |
| Cl              | nil   | trace | trace |
| P               | trace | trace | trace |
| pH              | 6.0%  | 6.0%  | 6.0%  |

From the results the corrosion coatings (scales) are basically composed of the typical galvanized compounds, CaCO<sub>3</sub>, plus Zn(OH)<sub>2</sub>. The presence of Cu, added to the test waters, is indicated for each coating. No reason or explanation for the higher Cu content in the K (Korean) pipe coating can be offered by the author at this time.

D. Chemistry, Coatings, Scanning Electron Microscopy (SEM)

EDX (Energy Dispersive X-Ray) Scans

1. EDX scans were conducted on bulk coating samples. In general, the results did not provide any additional information to that presented by the light spectroscopy. However, the higher Cu content in the K (Korean) coating sample found by light spectroscopy, was not apparent on the EDX graphs. It should be noted that both the light spectroscopy and EDX methods utilized for the coating analyses are semi-quantitative. EDX scans are presented, Figures 6, 7 and 8.
2. SEM and EDX studies were conducted for particulate metallic matter observed in the coating. The particles proved to be primarily Fe (EDX), with irregular shapes, such as slivers and shavings (SEM), observed in the visual examinations.

E. Microscopy

Sample sections were prepared for each pipe manufacturer (K, A, U), unexposed and exposed to water test conditions (outlined above). Following microscopic studies by the author, photomicrographs were printed of typical coating details at 450X size (enclosed Figures 9 - 16), identified below.

Photomicrographs, Galvanized Steel Pipe

MWDSC Samples

| <u>Manufacturer</u> | <u>Unexposed</u>            | <u>Exposed</u> |
|---------------------|-----------------------------|----------------|
| K (Korean)          | Figure 11, 14<br>(weld-40X) | Figures 9, 10  |
| A (Australian)      | Figure 12                   | Figure 15      |
| U (USA)             | Figure 13                   | Figure 16      |

Comparisons between Figures 11, 12, and 13 reveal that the Sample K microstructure (Figure 11) is unique in that it includes a prominent separation at the base metal-coating interface. This condition is undesirable, as corrosion would be expected to develop prematurely at the discontinuity. There was no indication of the separation in the microstructures of A & U, Figures 12 and 13.

Figures 9 and 10 show the effects of the interface separation on the microstructure of K after the water test exposure. Again, this observed abnormality was not present in the microstructures of exposed samples A & U, Figures 15 and 16. Although development of the interface discontinuity is apparent for the exposed K sample, the separation on this particular Section (Figures 9 and 10) is not as pronounced as that for the unexposed sample (Figure 11). The exact cause of the interface problem was not studied; still, the discontinuities observed in the Korean pipe (exposed, unexposed) are considered indicative of deficient coating integrity, leading to premature corrosion effects.

Full cross-sections of each unexposed pipe sample were prepared to reveal characteristics of the grain structures through the wall thickness for 360°. Studies were made in the etched and unetched conditions at high magnification (450X). Sample K showed definite evidence of welded construction (longitudinal seam), but A & U did not. Figure 14 shows the weld "flash" at the I.D. of K, revealing two discontinuities in the weld protrusion:

- A. Irregular "mushroom" shape of flash (Figure 14)
- B. Fissuring in weld under mushroom head (arrow).

Examination of grain structures in the butt joint connection showed no discontinuities in the weld material under the flash.

The geometry of the observed mushroom protrusion produces an annular space under the head that presents reliability problems in galvanizing. The weld fissuring provides additional potential origins for corrosion cells.

F. Thickness Measurements, Galvanized Coatings

Galvanized coating thickness values were (roughly) obtained by microscopic examinations, scanning prepared sections in several zones, employing a vernier scale.

Thickness, MWDSC Galvanized Steel Pipe

|                | Unexposed     | Exposed        |
|----------------|---------------|----------------|
| K (Korean)     | .002" - .006" | .0015" - .004" |
| A (Australian) | .002" - .004" | .002" - .004"  |
| U (USA)        | .005" - .008" | .001" - .004"  |

Although the above data are not offered as an accurate survey, the impression is that the U (USA) pipe sample furnished has the thickest galvanized coating, as manufactured.

#### Observations

1. The results show that no significant corrosion occurred for any of the MWD water test exposed samples.
2. The chemical compositions of the sample pipes were quite similar, except for carbon, which varied from very low in the Korean material (.03%) to more typical "low carbon" levels in the Australian and USA pipes (.12-.14%).
3. The corrosion coatings showed no discrete contaminants or significant particulate matter. The element copper was evidently dissolved in the scale to levels of .15-.40%. Higher aluminum values than expected are thought to be caused (possibly) by pickup from filter alums leaked by the test waters.
4. From the pipe studies, variations between the K, A and U base metal chemical compositions are not thought to be significant in relation to protective coating formations, or to corrosion effects.
5. There was an abnormal condition in the Korean pipe galvanized coatings which developed a discontinuous or separated layer at the Fe-Zn alloy to base metal interface.

This lack of integrity in the coating is expected to cause premature corrosion. In addition, a weld flash in this pipe was observed to present more discontinuities, in the form of an undesirable shaped protrusion which also contained fissures.

6. Although no pronounced attack was in evidence, it is believed that more stringent exposure conditions would probably cause premature corrosion of the Korean material. These conditions would especially relate to higher temperatures, and longer exposure times.

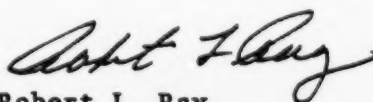
Further, other galvanized pipe manufactured by the same Korean source, or manufactured by the same methods and controls may develop more severely formed discontinuities than those described, due to variables of production.

7. The K sample pipe, identified as "Korean manufacture", appears to be unique among the samples tested:

- A. K is the only sample pipe which reveals manifestations of welded construction.

- B. K is the only sample pipe which shows deficiencies in the galvanized coating.

8. It should be noted that A and U pipe samples could also have been manufactured by seam welding, but masked from weld identity by flash removal and metallurgical (thermal) processing.



Robert L. Ray  
MtE #321

RLR:mb

Encl.: Figures 1 - 16



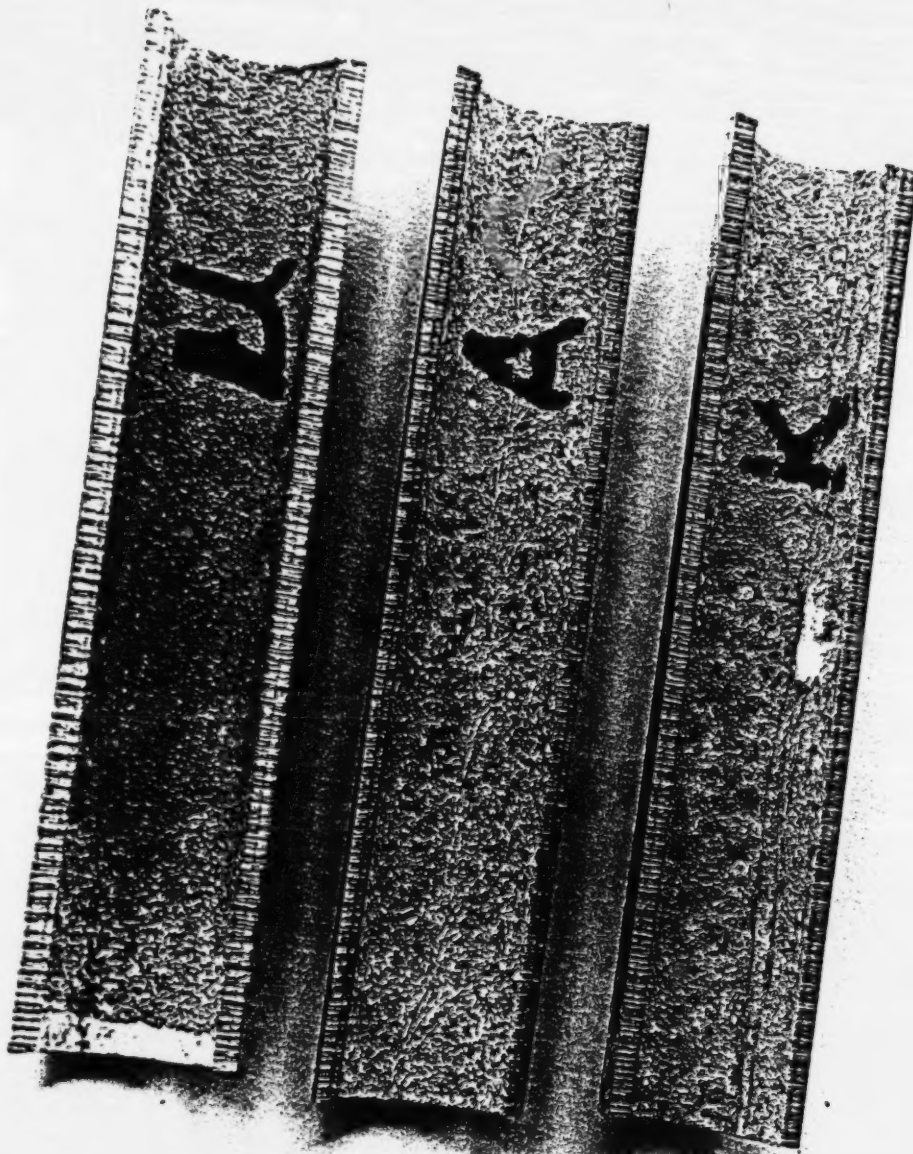


FIGURE 1  
Exposed sample pipe sections received for studies "K", "A", and "U".

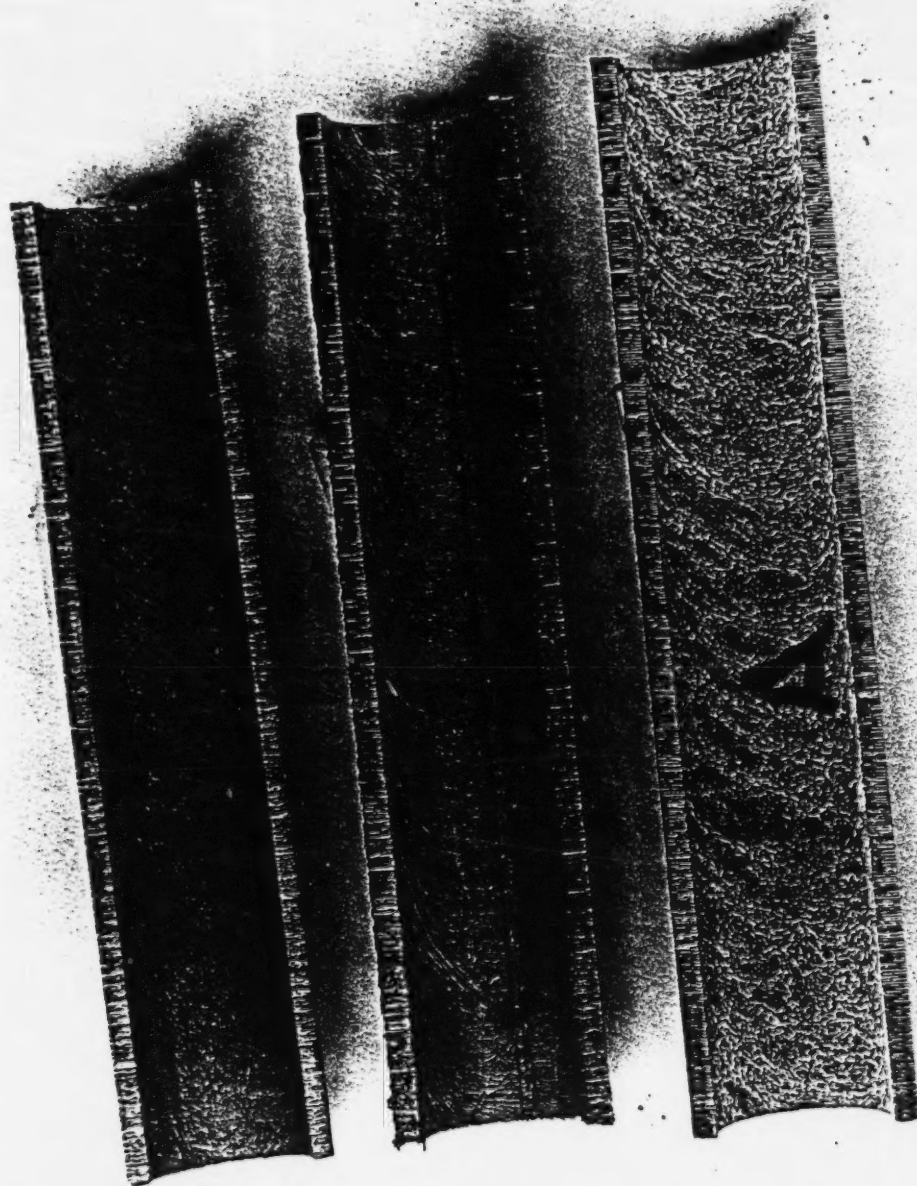
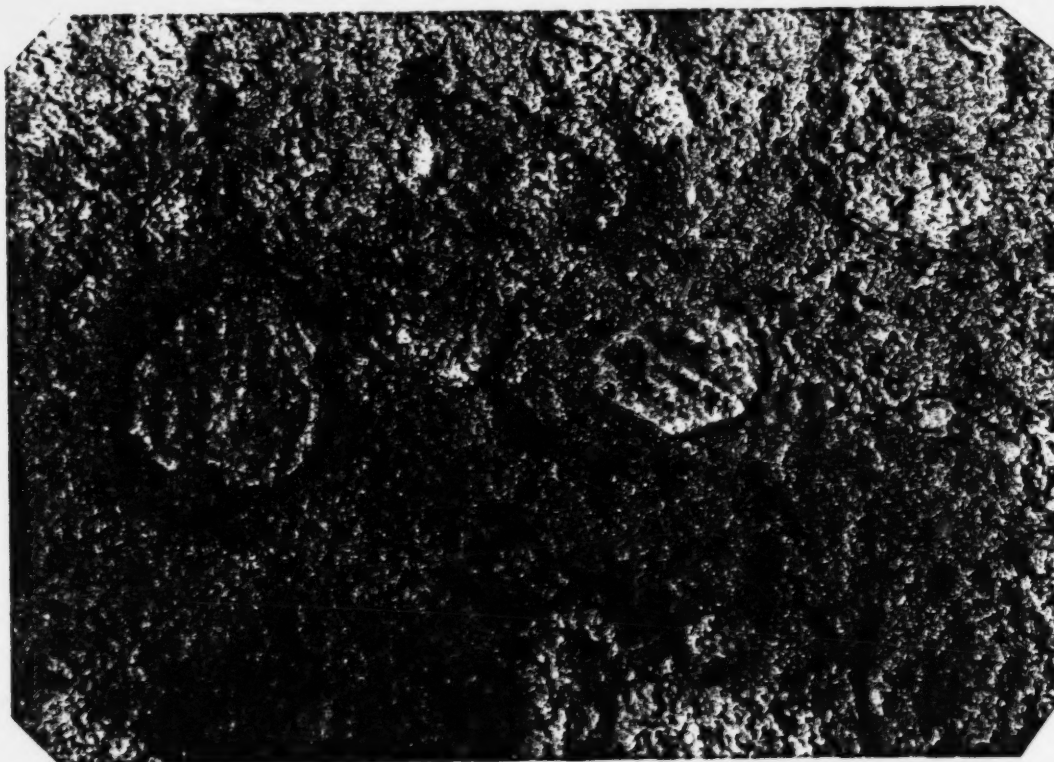


FIGURE 2

"New" sample pipe sections, indicating weld seam (X).

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FIGURE 3  
MWDSC WATER EXPOSED GALVANIZED STEEL PIPE  
KOREAN PIPE (K), SURFACE STRUCTURE I.D.



25X Size

Photomicrograph shows typical structure of this pipe interior after MWD test water flow. The exposed surfaces were studied by SEM, EDX, and light spectroscopy, as reported in the text. No significant discrete metallic particles were found and Cu content in the bulk coating ranged from .15 - .40% (by spectroscopy). The brown coloration is attributed to the presence of Fe-H<sub>2</sub>O compounds.

Close inspection of this photomicrograph (or Figures 4 and 5) may reveal small shiny particles. As explained in the text, these were found to be insignificant (steel shavings from sawcuts). Pits (arrow) are .040" - .060" diameter, and probably represent loose coating areas. This effect is less pronounced for sample "A". Figure 4.



J. F. Thomas, Ph.D.

FIGURE 4

MWDSC WATER EXPOSED GALVANIZED STEEL PIPE  
AUSTRALIAN PIPE (A), SURFACE STRUCTURE I.D.



25X Size

As reported, the corrosion scale for this sample (A) was quite similar in composition to those for the K and U exposed pipes. Small pits, observed for K and U samples, are not evident for this surface. However, the coating does show some intermittent characteristics.

J. F. Thomas, Ph.D.

FIGURE 5

MWDSC WATER EXPOSED GALVANIZED STEEL PIPE  
USA PIPE (U), SURFACE STRUCTURE I.D.

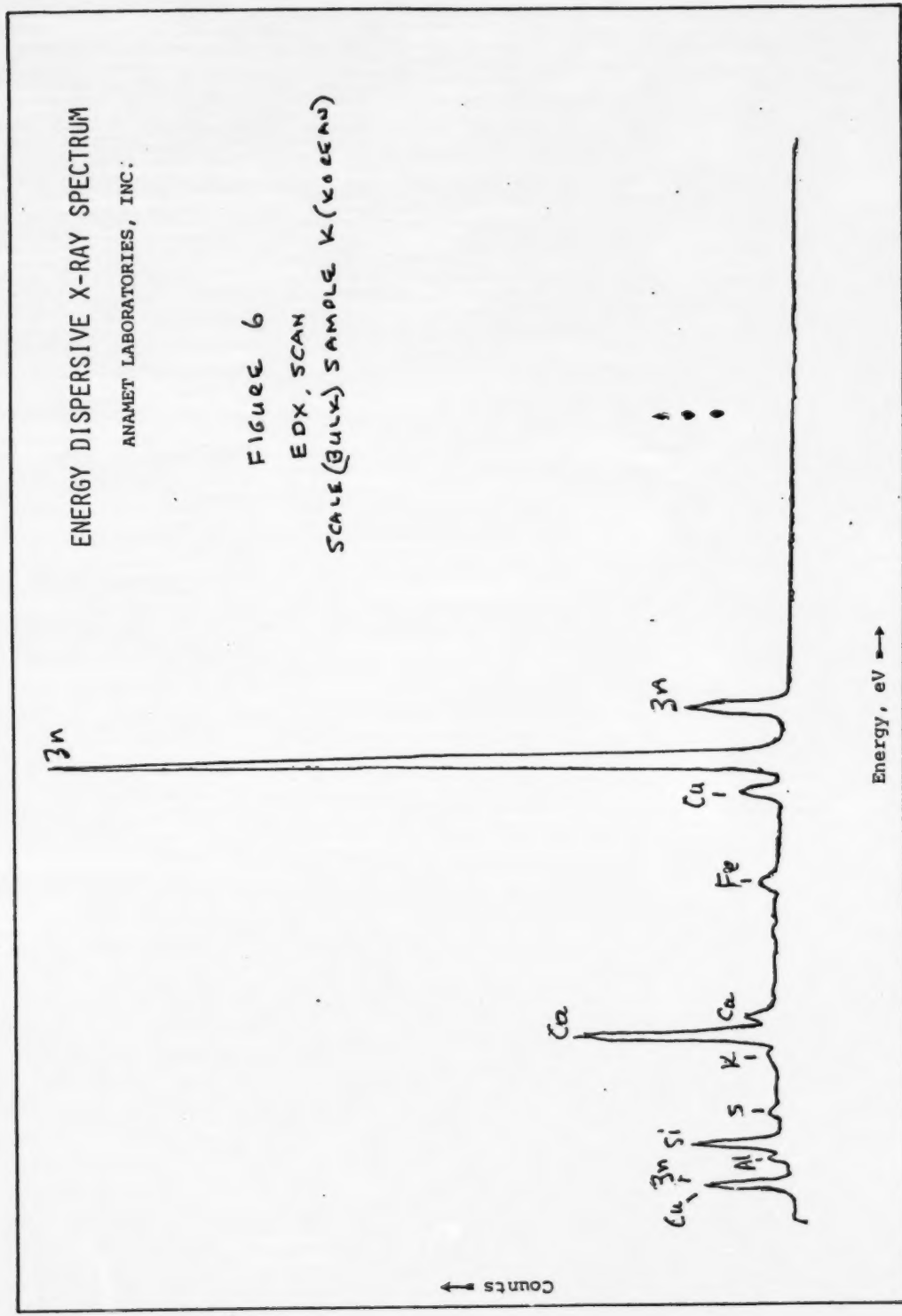


25X Size

Small pits, observed on pipe K, are also characteristic of this coating. As reported in the text, corrosion layer for this sample was approximately .004" thickness.



Customer R. L. Ray Lab. No. 1083. 203 Spectrum ID K 337



Customer K. L. Kay Lab. No. 1083.203 Spectrum ID 44826

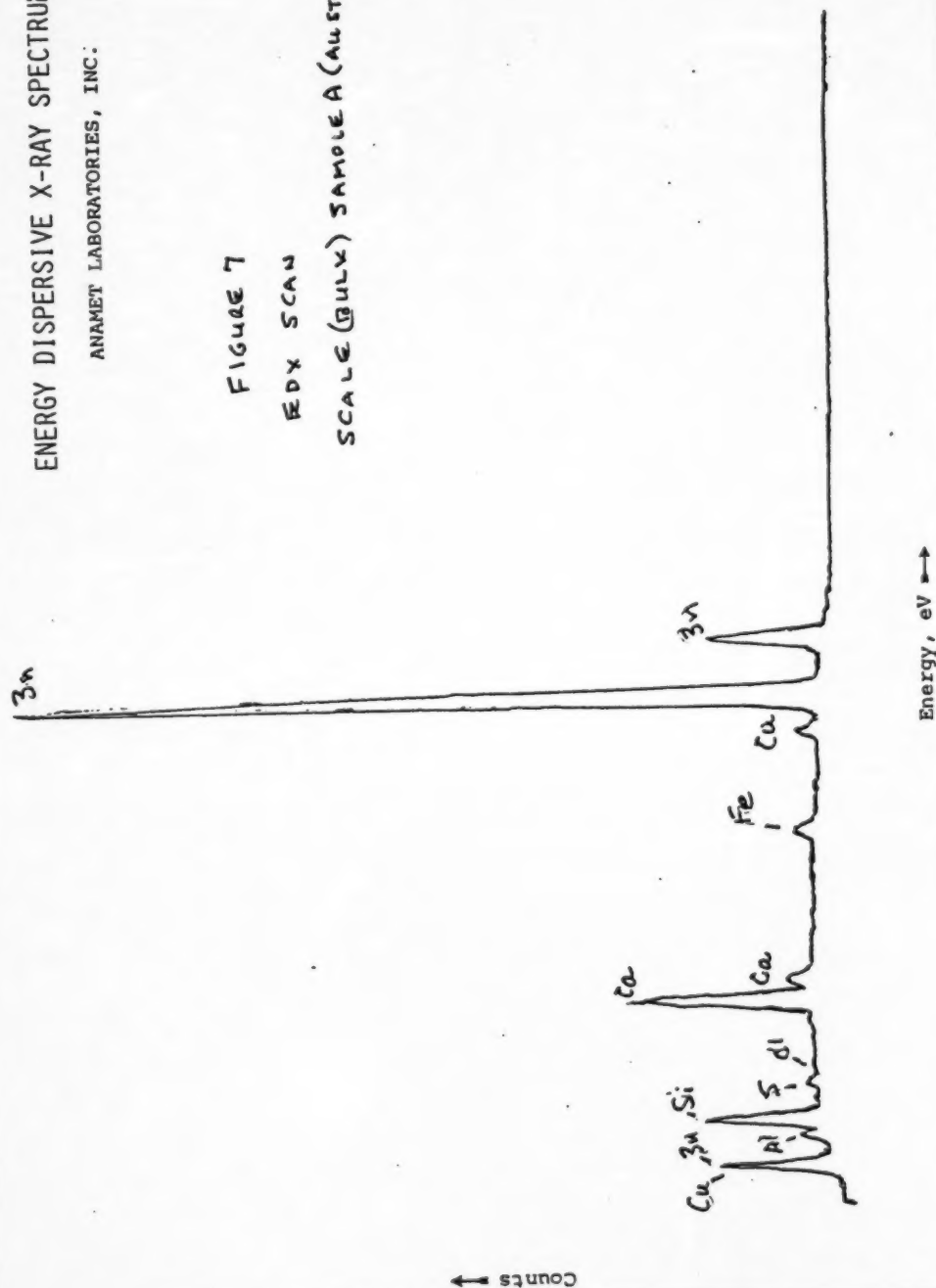
# ENERGY DISPERSIVE X-RAY SPECTRUM

ANAMET LABORATORIES, INC.

FIGURE 7

EDX SCAN

SCALE (GULF) SAMPLE A (AUSTRALIAN)



Customer R-L Ray Lab. No. 1083.203 Spectrum ID U51D

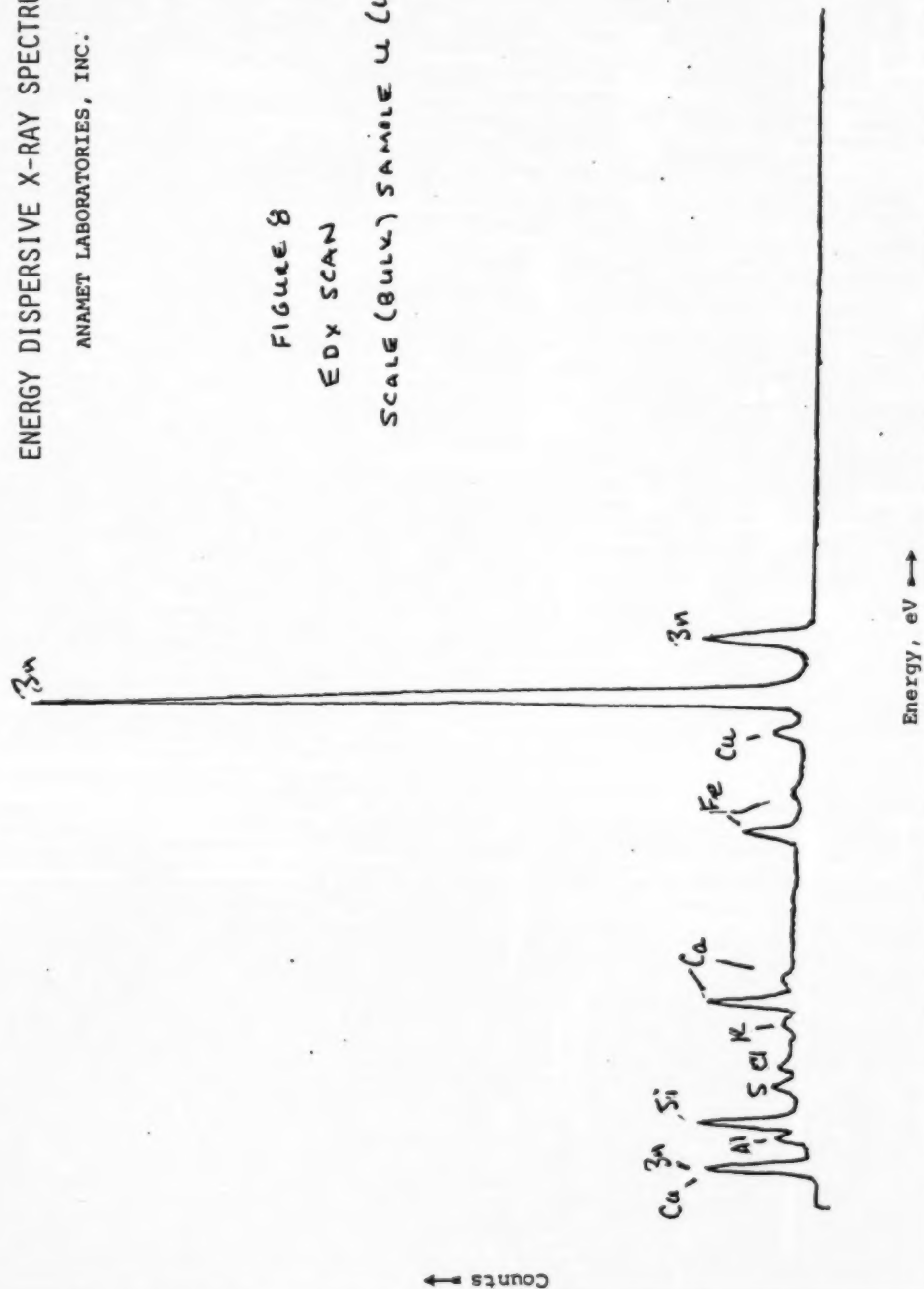
# ENERGY DISPERSIVE X-RAY SPECTRUM

ANAMET LABORATORIES, INC.

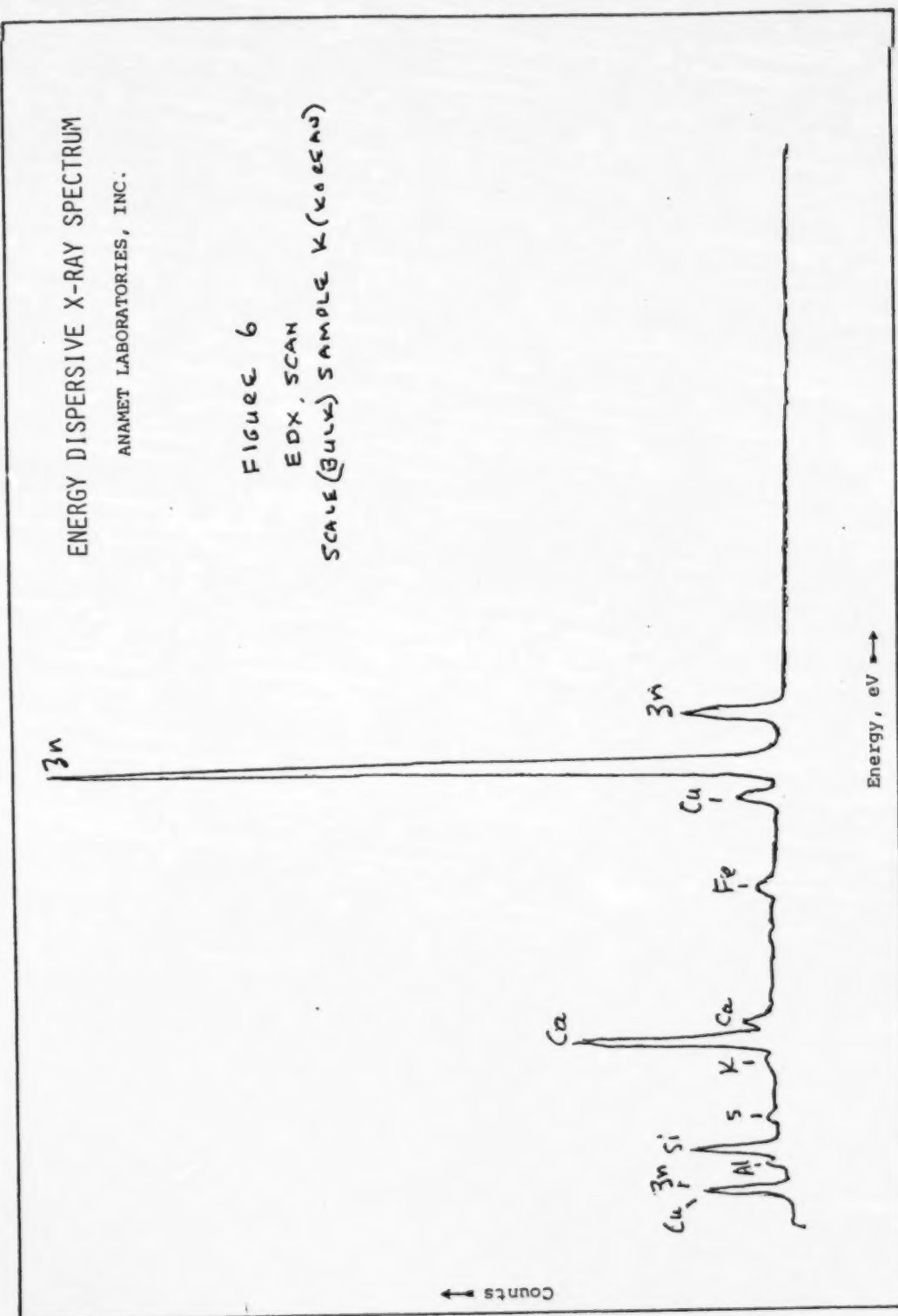
FIGURE 8

EDX SCAN

SCALE (BULK) SAMPLE U (USA)



Customer R. L. Ray Lab. No. 1083.203 Spectrum ID K337



Customer R. L. Ray Lab. No. 1083.203 Spectrum ID A 4826

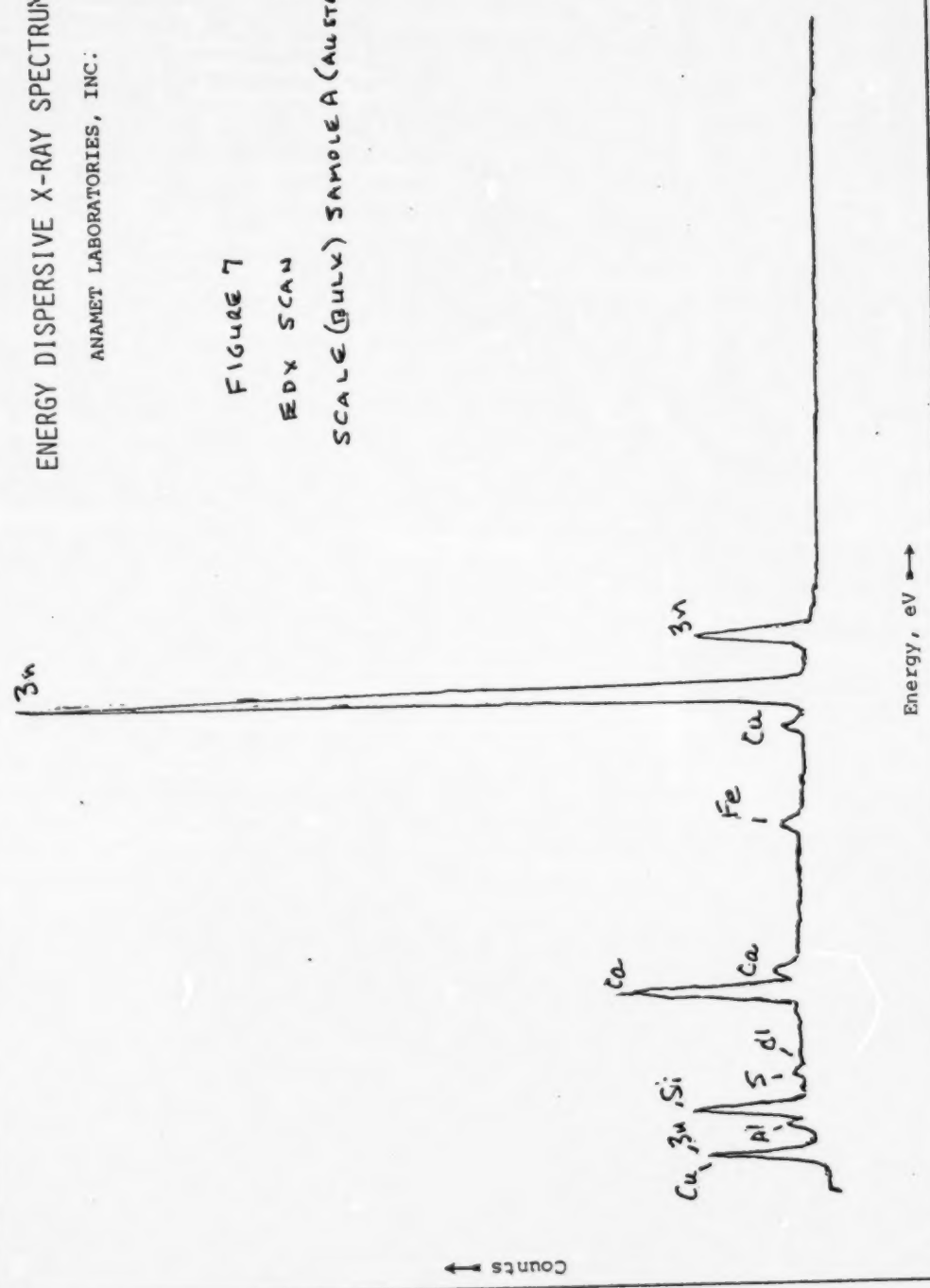
ENERGY DISPERSIVE X-RAY SPECTRUM

ANAMET LABORATORIES, INC.

FIGURE 7

EDX SCAN

SCALE (BULK) SAMPLE A (ALUMINUM)





Customer R.L. Ray Lab. No. 1083.203 Spectrum ID U510

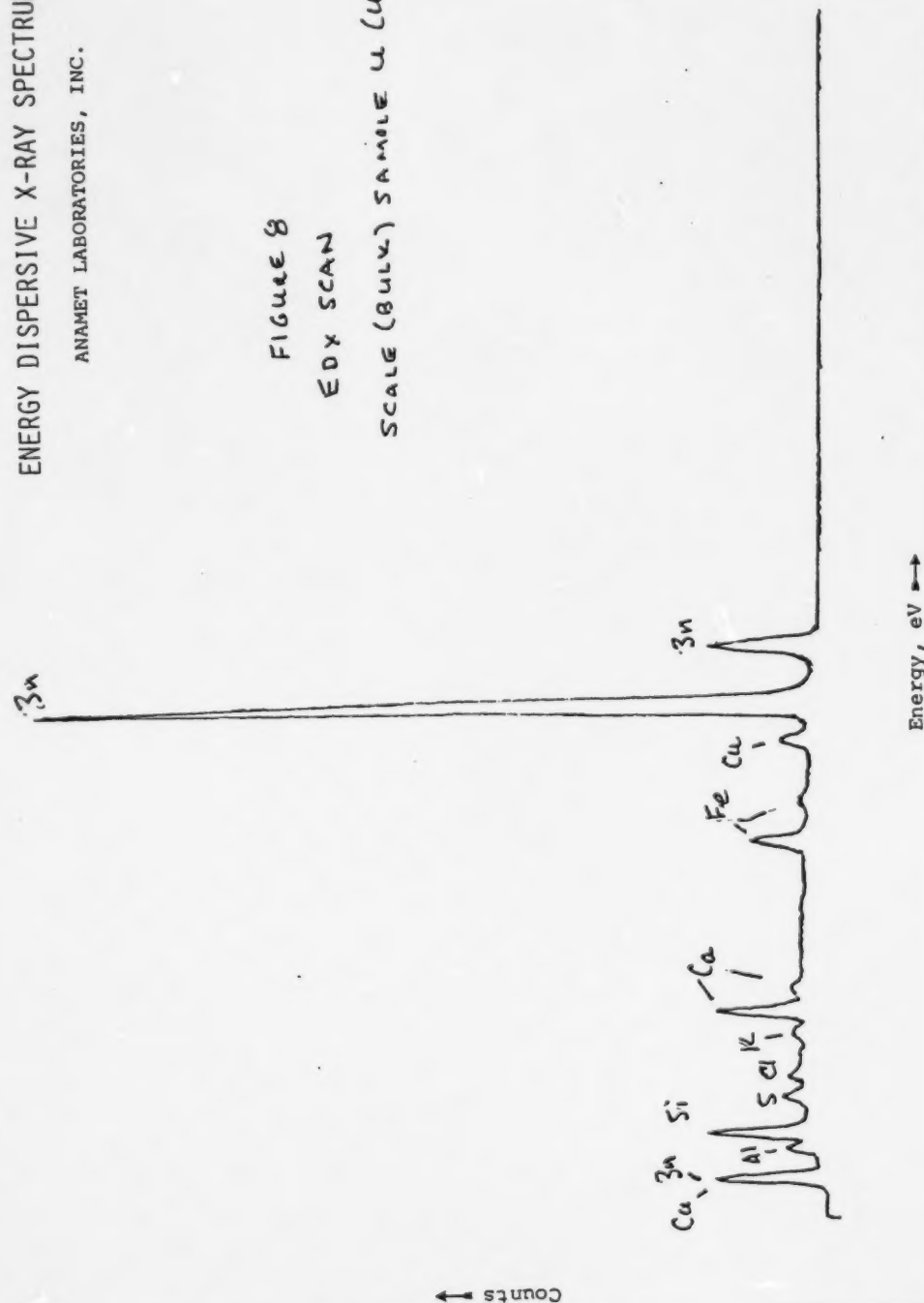
ENERGY DISPERSIVE X-RAY SPECTRUM

ANAMET LABORATORIES, INC.

FIGURE 8

EDX SCAN

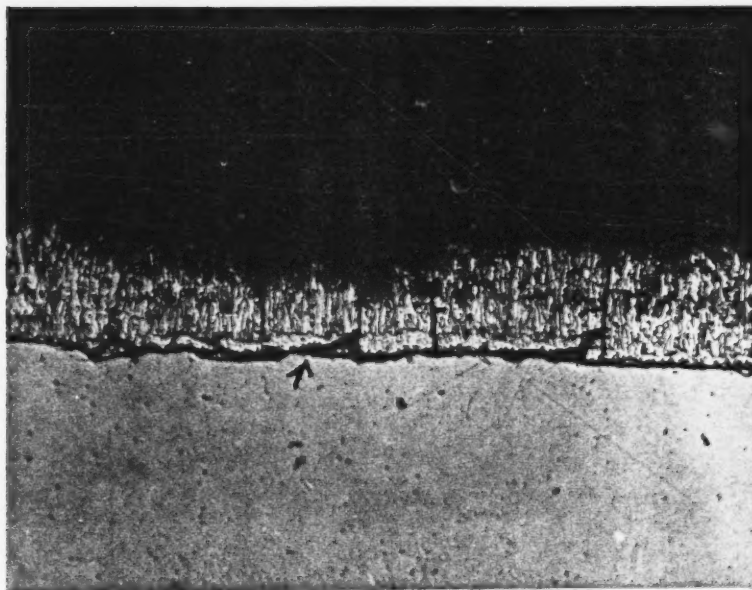
SCALE (BULK) SAMPLE U (USA)



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FIGURE 9

METALLOGRAPHY, WATER EXPOSED GALVANIZED PIPE  
KOREAN (K) SAMPLE I.D., ETCHED MICROSTRUCTURE



450X

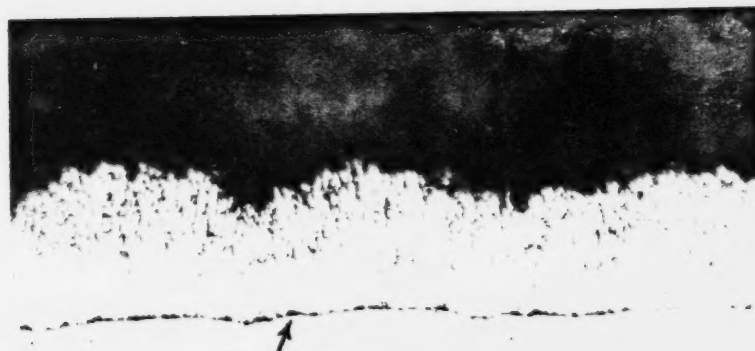
Nital Etched

Fe - Zn alloy-base metal interface has abnormal layer (arrow), thought to be related to separation and/or to corrosion attack resulting from the discontinuity before exposure. The abnormality is also illustrated by observing the unetched microstructure, Figure 10, and the unexposed condition, Figure 11. The observed abnormal condition was not present in the microstructures of Samples A and U, Figures 7.

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FIGURE 10

METALLOGRAPHY, WATER EXPOSED GALVANIZED PIPE  
KOREAN (K) SAMPLE I.D. UNETCHED MICROSTRUCTURE



450X

Unetched

Interface abnormality appears as somewhat discontinuous deposits in the unetched microstructure. Thickness of the galvanized coating was measured (vernier scale) to be .0015" - .004" for this water test exposed sample.

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FIGURE 11

METALLOGRAPHY, UNEXPOSED (NEW) GALVANIZED PIPE  
KOREAN (K) SAMPLE I.D. UNETCHED MICROSTRUCTURE



450X

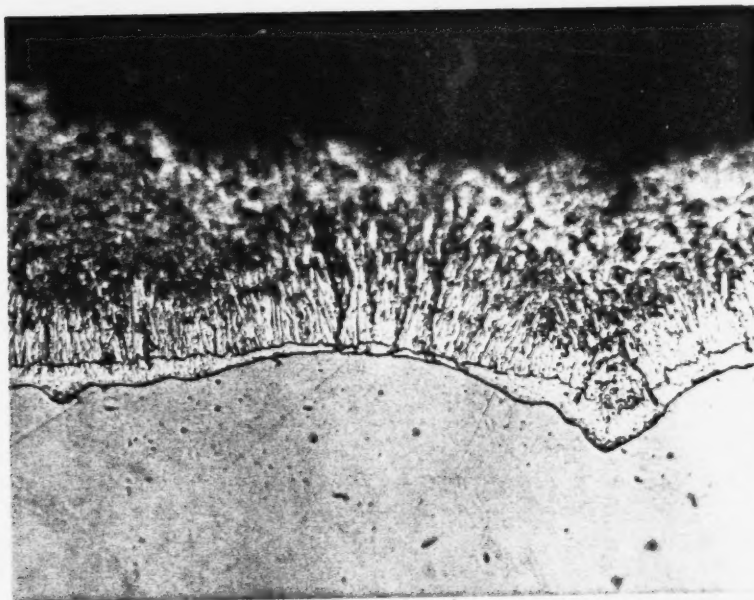
Nital Etched

"New" galvanized Korean pipe shows a separation zone at the base steel to Zn - Fe alloy interface. The cause of this condition, related to the galvanizing process details, is not known, requiring further studies for explanation. Coating thickness was measured to be .002" - .006" for this material.

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FIGURE 12

METALLOGRAPHY, UNEXPOSED (NEW) GALVANIZED PIPE  
AUSTRALIAN (A) SAMPLE I.D. ETCHED MICROSTRUCTURE



450X

Nital Etched

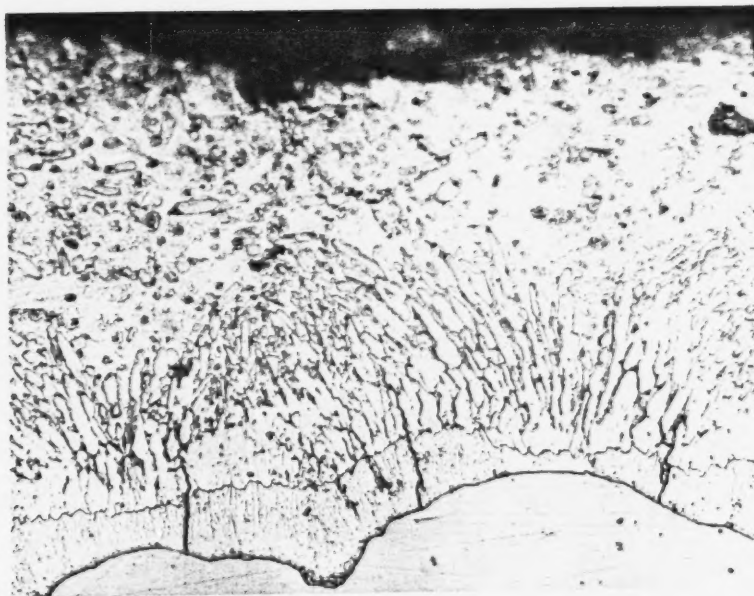
Normal galvanized coating is evident for the new "A" sample (prior to the MWD water exposure cycles). Coating thickness was measured to be .002" - .004".



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FIGURE 13

METALLOGRAPHY, UNEXPOSED GALVANIZED PIPE  
USA (U) SAMPLE I.D. ETCHED MICROSTRUCTURE



450X  
Nital Etched

Normal galvanized coating is evident for the "U" sample before MWD  
water exposure cycles. Coating thickness was measured to be .005"  
- .008".

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FIGURE 14

METALLOGRAPHY, UNEXPOSED (NEW) GALVANIZED PIPE  
KOREAN (K) SAMPLE I.D. ETCHED MICROSTRUCTURE  
WELD ZONE



40X

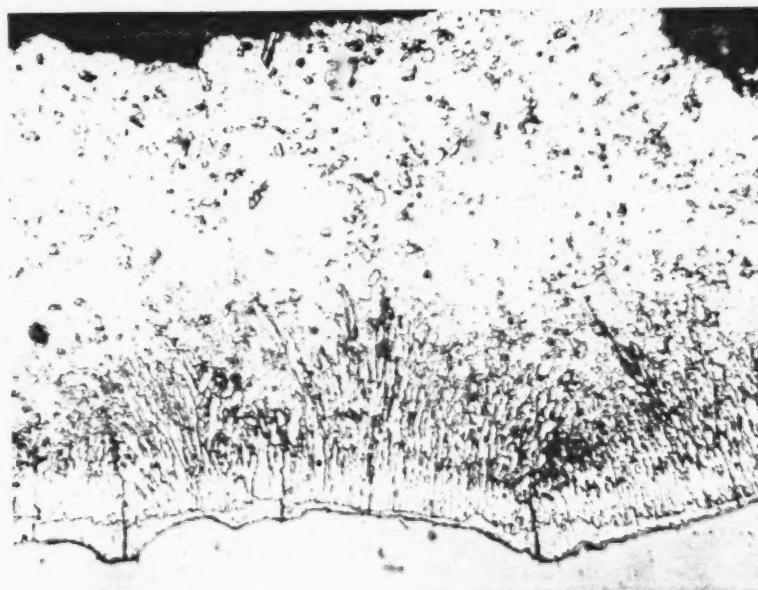
Nital Etched

"New" galvanized Korean pipe microstructure is shown at weld zone. The discontinuities at the weld flash are considered detrimental to corrosion resistance. The author has observed galvanized pipe failures (corrosion) originating at these zones and progressing through the wall thickness. Sample pipes "A" and "U" were searched (microscopically) for similar weld zones, and none were found.

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FIGURE 15

METALLOGRAPHY, WATER EXPOSED GALVANIZED PIPE  
AUSTRALIAN (A) SAMPLE I.D. ETCHED MICROSTRUCTURE



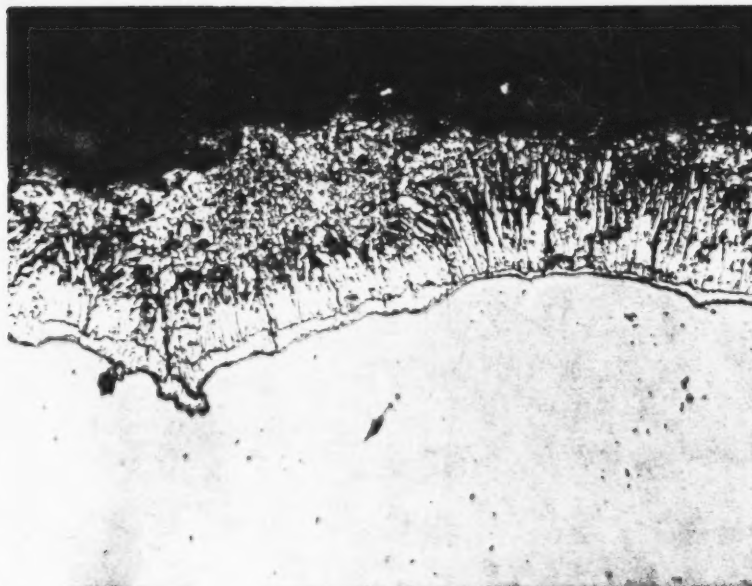
450X  
Nital Etched

Australian pipe shows little loss of Zn coating after MWD water test exposure. Galvanized characteristics are normal and thickness at the zone illustrated is .005". General thickness measured was .002" - .004".

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FIGURE 16

METALLOGRAPHY, WATER EXPOSED GALVANIZED PIPE  
USA (U) SAMPLE I.D. ETCHED MICROSTRUCTURE



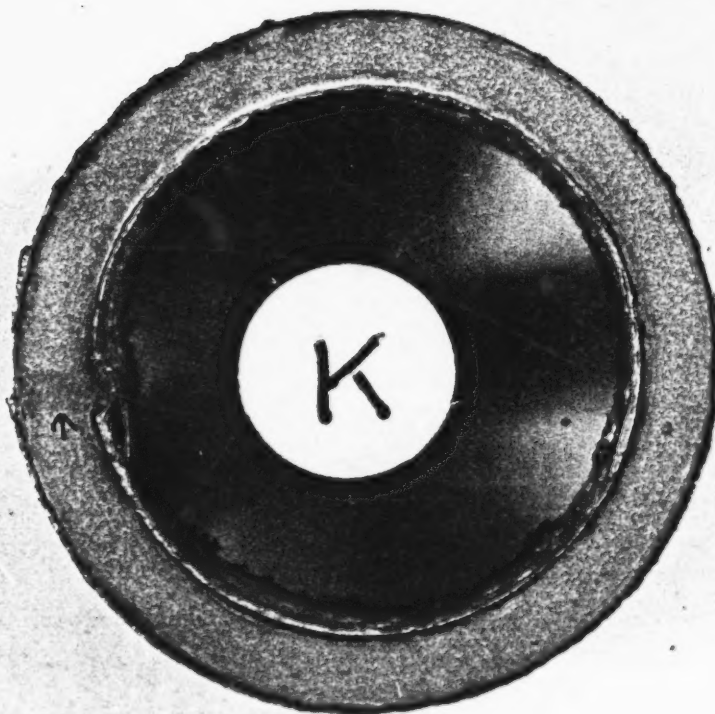
450X

Etched

USA pipe shows typical galvanized characteristics after MWD water test exposure. Thickness of galvanized layer was measured to be .001" - .004".

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FIGURE 17  
MWDSC  
"KOREAN" GALVANIZED STEEL PIPE, TRANSVERSE SECTION  
PHOTOMACROGRAPH



4X Ammonium Persulfate Etch Preparation and etch shows weld seam and protrusion (flash) discontinuity (arrow). Microscopic characteristics of the protrusion are illustrated in the photomicrographs, Figures 14 and 20.



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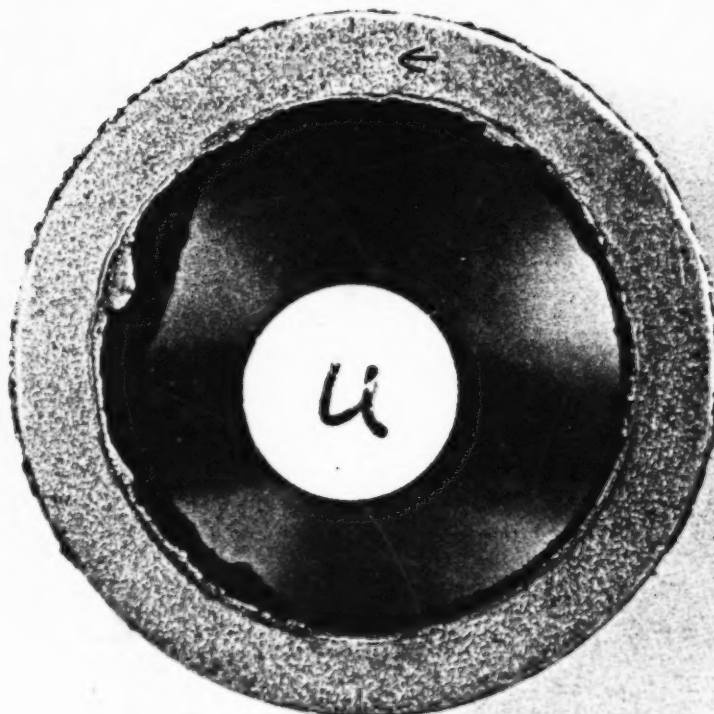
FIGURE 18  
MWDSC  
"AUSTRALIAN" PIPE, TRANSVERSE SECTION  
PHOTOMACROGRAPH



4X Ammonium Persulfate Etch Preparation and  
etch do not show any vestige of weld seam.

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FIGURE 19  
MWDSC  
"USA" GALVANIZED STEEL PIPE, TRANSVERSE SECTION  
PHOTOMACROGRAPH

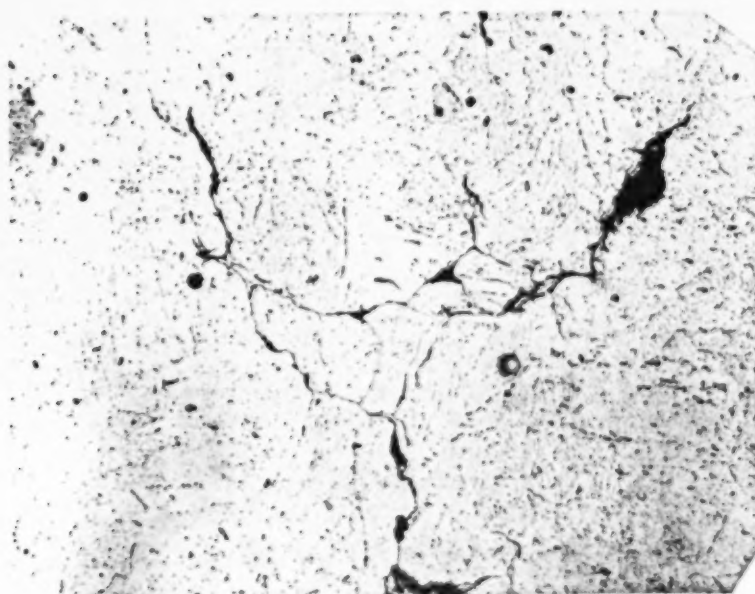


4X Ammonium Persulfate Etch Preparation and strong effects of etch show faint vestige of probable weld seam (arrow). High magnification microscopic studies (through the pipe wall in this zone) did not disclose weld effects in the grains.

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FIGURE 20

METALLOGRAPHY, UNEXPOSED (NEW) GALVANIZED PIPE  
KOREAN (K) SAMPLE I.D. ETCHED MICROSTRUCTURE  
WELD ZONE  
HIGH MAGNIFICATION VIEW



450X

Nital Etched

"New" galvanized Korean pipe microstructure is shown at weld zone. The discontinuities at the weld flash are considered detrimental to corrosion resistance. The author has observed galvanized pipe failures (corrosion) originating at these zones and progressing through the wall thickness. Sample pipes "A" and "U" were searched (microscopically) for similar weld zones, and none were found.